PERFORMANCE EVALUATION OF POLYMER MODIFIED CEMENT MORTARS AT DIFFERENT EXPOSURE CONDITIONS

A THESIS

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Dedicated to,

Amma & Acha

THESIS CERTIFICATE

This is to certify that the thesis titled "**PERFORMANCE EVALUATION OF POLYMER MODIFIED CEMENT MORTARS AT DIFFERENT EXPOSURE CONDITIONS**" submitted by **Aswathy Rajendran**, to the Department of Civil Engineering, Indian Institute of Technology Madras, Chennai, for the award of the degree of Master of Science is a bona fide record of research work carried out by her under my supervision. The contents of this thesis, in full or in parts, have not been submitted and will not be submitted to any other Institute or University for the award of any degree or diploma.

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ABSTRACT

KEYWORDS: Polymer modified mortars (PMMs), curing, exposure conditions, porosity, water permeability, shrinkage

Polymers as additives find a role in various civil engineering applications, such as repairing, waterproofing and flooring. The interaction of polymers with cementitious systems generally results in the formation of a continuous matrix of polymers and the hydration products. Literature suggests that the interaction of polymers with cement can induce pore refinement, which increases durability properties, specifically in terms of resistance to chemical ingress. In addition, Polymer Modified Mortars (PMMs) could have better workability, toughness and bonding with the substrate than a conventional mortar system. However, these beneficial properties of PMMs could be dependent on the type of curing and exposure conditions due to their influence on the interaction of the polymers with the binder system. Many polymeric systems used in construction applications have given lower than expected performances due to the lack of understanding of such influencing factors that govern the performance of the PMMs, along with poor construction practices.

In this study, several factors affecting the performance of PMMs have been investigated, considering a range of applications and exposure conditions to which the polymeric systems could be subjected during the service life. Three objectives were consequently defined: firstly, to study the influence of curing and weathering on the performance of PMMs; secondly, to assess the performance of PMMs after exposure to elevated temperatures; and thirdly, to assess the combustibility and flammability of the PMMs when exposed to fire. Three major types of the polymeric systems are considered in this study: two conventional polymeric latexes (Styrene Butadiene Rubber, SBR and Poly-Acrylic Ester, PAE), and a recently formulated water-based silane polymer emulsion (SIL). These systems have been added as integral additives in cementitious mortars to investigate their performance. The dosages of the three polymers were selected based on the recommendations of the manufacturers. To better understand the mechanisms of these systems and characterize the effects on microstructure, a higher than recommended dosage of 10 % polymer solid to cement ratio (p/c) was also chosen for the SBR and PAE systems. In the case of the SIL systems, the primary dosage studied had a 0.25 % emulsion to cement ratio (e/c). The low dosage was chosen keeping in mind the cost involved, as well as the results from preliminary studies. However, higher dosages have also been assessed to a limited extent.

The mortars have been subjected to three types of curing, categorized based on the duration: Type 1: 1 day of wet curing followed by air curing at 25 °C and 65 % relative humidity; Type 2 curing: 7 days of wet curing followed by air curing at 25 °C and 65 % relative humidity and, Type 3: 28 days of wet curing. To understand the effects of curing, the following parameters were assessed: (i) compressive strength (ii) flexural strength (iii) drying shrinkage, (iv) water permeability, and (v) microstructural features using Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD) and Mercury Intrusion Porosimetry (MIP). The evaluation of these characteristics was also done after subjecting the mortars to accelerated weathering, in a specially-fabricated chamber, consisting of cycles of 8 hours under ultraviolet radiation and 4 hours under high humidity, for 30 days.

From the test results, it was found that the dosage of polymer, curing type and exposure conditions significantly influence the properties of the cementitious system. Polymers such as SBR and PAE were found to be more sensitive to curing period, while SIL mortars had lesser variations in performance with different curing conditions. At normal conditions, the mechanical properties were better in the SIL mortars, while SBR modified mortars had enhanced resistance against shrinkage and water permeability.

For all three polymeric systems, 7 days of wet curing followed by air curing was found to yield higher mechanical properties than the other curing conditions. Shrinkage was also found to be lower with limited wet curing and increased progressively when longer wet curing was adopted. On the other hand, water permeability was found to improve with extended periods of wet curing. It was also seen that employing higher dosages of PAE polymers had a detrimental effect, unlike in the SBR polymers. Leaching of the polymer was also noticed at higher dosages of PAE when subjected to longer wet curing periods, along with higher shrinkage and water permeability.

After accelerated weathering, the performance of the polymeric systems followed the order of SIL > PAE > SBR, for all properties. Weathering was found to adversely affect the water permeability more than the mechanical properties of the polymeric systems. The retention of properties in SIL mortars suggests that it could be a good choice for outdoor applications, such as in plastering and overlays. SBR mortars had lesser resistance to weathering compared to the other mortars.

On exposure to elevated temperatures, SIL mortars were found to be more stable though none of the systems retained more than 50% of strength above 300°C, along with a significant increase in porosity. None of the mortars were found to be combustible or flammable, as observed after subjecting them to 1000 °C for one hour.

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CHAPTER 1

INTRODUCTION

1.1 Background

Polymer modified mortars (PMMs) find applications in a variety of domains such as repair, waterproofing, adhesives, grouting and overlays on floorings and pavements. The distinct mechanism of polymer film formation in the cementitious matrix, binding the system effectively against external chemical ingress, provides enhanced durability in such applications. Addition of polymers in a cementitious system improves workability, bond strength, toughness, and durability, though often at the expense of reduced mechanical properties. Unlike an unmodified cementitious mortar (UCM), PMMs are found to be more susceptible to wet curing and exposure conditions (UV, humidity, temperature) that needs to be accounted for while recommending polymeric system for various applications. Polymers are characterized by the polymer type (degree of crystallinity), which decides the major polymer characteristics and performance (glass transition temperature, melting point, UV resistance) at various critical exposure conditions. Thus, for any polymer modified mortar, the importance of the curing duration for the polymeric systems, and the alteration of performance under various exposure conditions need to be evaluated for the apt adoption of such systems.

1.2 Significance of research

Polymeric systems are being used widely in various civil engineering applications. However, it is broadly acknowledged that the dosages and curing types recommended by the manufacturers rarely address the needs of generic application of such systems. The product datasheets of the polymers rarely state the curing duration to attain the required performance, and the sensitivity of the polymeric systems to the exposure conditions are also not generally considered. Hence, it is important to develop suitable recommendations for the required performance of the PMMs with the adequate combination of dosage and curing for ensuring functionality during service. Also, a building material during its service life could be subjected to elevated temperatures during some unexpected events and to as high as 1000 °C in a fire, and consequently, it is necessary for the materials to retain adequate properties even after such exposure. This work focusses on the study of commonly used polymers in various applications of cement-based mortars, with different possible curing regimes and critical exposure conditions.

1.3 Objectives

The main objectives of this study are the following:

1. To study the influence of the wet curing period on the performance of PMMs, at normal conditions, and after exposure to accelerated conditions of weathering.

2. To evaluate the effect of elevated temperatures (up to 600 ºC) on the performance of PMMs.

3. To assess the combustibility and flammability of PMMs at elevated temperatures conditions (as high as 1000 °C, in accordance with the ISO 834 fire curve for building materials).

1.4 Scope and methodology adopted for the study

(i) A water to cement (w/c) ratio of 0.45 and cement to sand (c/s) ratio of 1:3 were adopted for casting of mortars, as they are considered typical in various applications.

(ii) Polymer latexes such as styrene butadiene rubber (SBR) and polyacrylic ester (PAE) and a silane modified emulsion polymer (SIL) were considered for the study.

(iii) Three curing types were adopted: 1-day wet curing followed by air curing at 25 °C and 65 % relative humidity (designated as Type 1), 7 days of wet curing followed by air curing at 25 °C and 65 % relative humidity (designated as Type 2), and 28 days of wet curing (designated as Type 3).

(iv) PAE and SBR mortars were tested with polymer solid to cement (p/c) dosages of 4.5% (following the recommendations of the manufacturers) and 10% (which is the minimum required for effective polymer film formation, as reported in literature). For the silane systems an emulsion to cement (e/c) dosage range of 0.25 % to 3 %; 0.25 % was recommended by the manufacturer and other higher dosages were selected to study the influence of dosage on the PMM behaviour) was used.

The parameters and the methodology adopted for the study are shown in the flow chart in Figure 1.1.

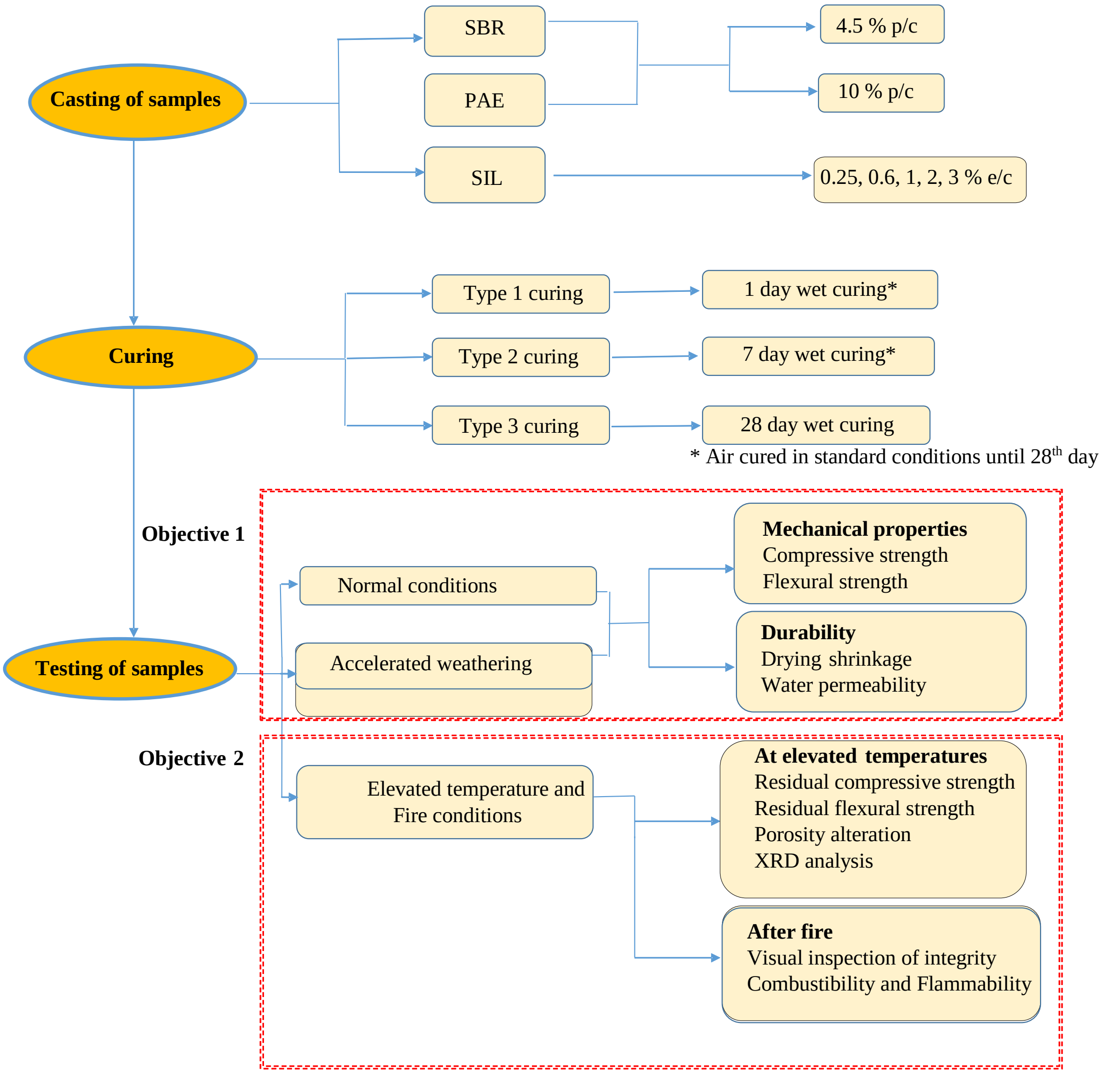


Figure 1.1: Flowchart representing the methodology adopted for the study

As discussed, three polymer modified mortar systems at different dosages are subjected to various conditions, and evaluated for the properties. Testing was carried out at normal conditions (after the specified curing periods), after exposure to accelerated conditions of weathering (i.e., after the specified curing periods, specimens were subjected to accelerated weathering conditions), and at elevated temperature and fire conditions.

1.5 Organization of thesis

The thesis is organized as 8 chapters as follows.

Chapter 1 gives an introduction to polymer modified mortars, significance of research done, with the objectives and scope of study. The organization of the thesis into chapters is also presented.

Chapter 2 is a review of the work done previously on polymer modified mortars. It covers details of integral waterproofing, scope of polymers in integral waterproofing with the mechanism of polymer film formation; and influence of polymer modifications on cement mortar in terms of microstructure, fresh and hardened properties. Finally, the performance of polymer modified cement mortars at elevated temperature conditions and at fire are discussed in terms of residual properties (co-related with development of gas pressure) and spalling resistance of mortars.

Chapter 3 gives the details of the materials used for the study, the specifications followed for testing and the experimental procedures. The chapter also describes the procedures for the fabrication and testing of mortars with references to the codes followed.

Chapter 4 discusses the performance of polymer modified mortars at various curing types when tested at normal conditions. Performance evaluation is done based on the mechanical properties, water permeability, shrinkage and microstructural features (comprising of porosity and surface morphology) of the mortars.

Chapter 5 evaluates the performance of polymer modified mortars after exposure to accelerated conditions of weathering. The properties evaluated at normal conditions are re-evaluated after exposure to simulated conditions of aging and compared. The retention of the properties of mortars is assessed plotted for better understanding of the sensitivity of such systems to UV and humidity conditions.

Chapter 6 presents the results of tests on PMMs after subjecting them to elevated temperature conditions. The mechanical properties and porosity alteration at a range of elevated temperatures from 100 °C to 600 °C are evaluated for identifying the effect of exposure to high temperatures for such systems.

Chapter 7 evaluates the combustibility and flammability of PMMs at fire conditions systems. Analysis is done by visual inspection for understanding the loss of integrity in the mortar when subjected to conditions in a fire.

Chapter 8 summarizes the general conclusions and specific conclusions on the study done with scope for future work.

Appendix A discusses the details and results of testing done on fire resisting mortars that are used in the construction industry and could be the benchmark for the PMMs assessed here.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter discusses the research work done previously on polymer modified cement mortars and their performance evaluation. The review gives the details of polymeric systems as waterproofing systems and the use of polymers as integral waterproofing admixtures with the mechanism of polymer film formation. The influence of polymer modifications on the microstructure, fresh and hardened properties of cement mortar is also discussed in detail. Finally, the performance of polymer modified cement mortars at elevated temperatures is also discussed.

2.2 Waterproofing systems

Broadly, waterproofing systems can be grouped into four heads: (i) cement mortar improved by the addition of (integral) chemical or mineral admixtures; (ii) polymer modified cementitious systems; (iii) flexible membranes that can be applied as a liquid or a sheet; and (iv) coatings that are polymer based with or without cementitious components (Nair and Gettu 2014). Integral waterproofing systems refer to chemical admixtures or additives incorporated to the cement/concrete mixtures at the batch plant or jobsite to improve the resistance of the cementitious system against water ingress. They can be broadly classified as hydrophilic (water-loving) and hydrophobic systems (Borle and Ghadge 2016). Hydrophobic systems repel water from entering the concrete system. Alternatively, hydrophilic systems refer to admixtures that react with water and form crystalline products that fill the cracks and pores, thereby preventing further penetration of water.

The admixtures used for integral waterproofing are generally densifiers, repellents or crystalline admixtures (Manari and Kumar 2015). Densifiers are those materials that fill the pores in the hydrated cement system making it more dense and compact. Repellents form films and make the concrete system hydrophobic, and crystalline admixtures are those that are expected to result in the formation of crystalline products in the presence of water to seal the cracks and pores. Polymers are the most commonly employed class of repellents for waterproofing, as they have the extra advantage of increased workability and adhesion.

2.3 Polymer modified mortars (PMMs)

PMMs are ordinary cement mortars that have been modified with polymer additives, like latexes, re-dispersible powders, resins etc., to overcome the limitations of an ordinary cement mortar, such as lower tensile strength, higher water permeability and higher drying shrinkage. Polymer modification is found to improve the bond between cement paste and aggregate (Kim and Robertson 1998), and between the cement paste and steel fibres (Fu and Chung 1996). Thus, the combination of concrete and polymers can help exploit the improvement in properties of both, and yield cement composites with higher strength and durability (Kardon 1997). However, structural compatibility (e.g., bonding with the reinforcement) and thermal performance of PMMs could be different from conventional cement composites (Saccani and Magnaghi 1999), which may limit their application.

Most common forms of polymeric modifiers are listed below (Ohama 1995).

(i) Polymeric latexes
  a. Elastomeric latexes
  b. Thermosetting latexes
  c. Thermoplastic latexes
  d. Bituminous latexes
(ii) Re-dispersible polymer powders
(iii) Water soluble polymers
(iv) Liquid resins
(v) Monomers

As seen in the above list, polymers are generally added as re-dispersible powders or water-soluble polymers. Recently, prepacked polymer modified mortars have also been developed, where water can be directly added to dry blends consisting of polymer, binder and sand, addressing problems of mix calculations and improper addition of these admixture (Afridi et al. 2001; Saand et al. 2007). The disadvantage of adding polymers as re-dispersible powders is that the need for surface active agents, which could retard cement hydration and prevent the coalescence of polymer particles leading to inadequate polymer film formation (Beeldens 2002). When water-soluble polymers are used, in the absence of surface active agents, the polymer films are formed more easily and uniformly over the hydrates (Knapen et al. 2004). However, the sensitivity of PMMs to humidity limits their applications in some environments (Bikales 1971; Knapen et al. 2005).

Natural rubber, chloroprene rubber latex, styrene butadiene rubber, poly-acrylic ester latex, poly styrene-vinyl acrylic ester latex, epoxy resins and recently, silicone-based products are polymeric modifications that have been used in the construction sector. Fluoropolymers, which are commonly used in textile industry as fabric protectors, have also been proposed for waterproofing and found to have superior durability features than commercially available waterproofing agents (Krishnan et al. 2013). Other than their applications in waterproofing and repair mortars, fluoropolymers have also been recommended for bituminous mixes in pavements to achieve high fatigue resistance (Gupta and Veeraraghavan 2009). Many applications of fluoropolymers have shown promising potential for usage in combination with fibre reinforcement (Gerwick 1978; Soraushian et al. 1993; Zayat and Bayasi 1996) and in shotcrete (Schorn 1985).

The polymer latexes used for waterproofing and other applications are expected to meet the criteria, as suggested by Ohama (1995):

(i) Good mechanical stability to resist the shear stresses at the time of mortar mixing.
(ii) Good chemical stability to cations like Ca^{2+} and Al^{3+} that are produced during cement hydration.
(iii) Good thermal stability as they can be subjected to a range of temperatures during transportation and storage.
(iv) Continuity of the polymeric film formed with good adhesion to the cement hydrates and aggregates.
(v) Low air entrainment to avoid the need for antifoaming agents.

2.4 Mechanism of polymer interaction in cementitious systems

Effective polymer modification of cement mortar is governed by the rate of cement hydration and polymer film formation in the binder phase of the hydrates, formed prior to polymer film formation (Sakai and Sugita 1995; Fichet et al. 1998). PMMs have a co-matrix in which the polymer and cement matrix are homogenized, where the hydration of cement and polymerization of liquid resins and monomers occur simultaneously (Beeldens 2005; Bothra and Ghugal 2015). The basic mechanism of polymer film formation in mortars is given by Ohama's model, which is explained in stages with schematic representations (Figure 2.1).

Stage 1: When a polymer latex is incorporated in cement mortar, it gets uniformly dispersed in the cement phase. In the hydrating cement polymer paste, the polymer particles are partially deposited within the calcium silicate hydrate gel and on the unhydrated cement grains.

Stage 2: The polymer particles are initially confined in the capillary pores of the cementitious matrix. Later, with the progress of hydration, as more gel products are formed and more capillary water is consumed, the polymer particles coalesce to form a layer of closely packed particles over the hydration products, unhydrated particles and aggregates. The pores, in the sizes of picometers to nanometers in the mixture, get filled by these polymer particles, whose size generally ranges from 50 to 500 nanometers. Some chemical reactions are also expected to occur between the reactive polymers (polyacrylic esters, chloroprene rubber) and Ca^{2+} ions, calcium hydroxide and silicates of aggregates. These reactions are expected to improve the co-matrix formed and strengthen the bond between the aggregates and cement hydrates.

Stage 3: With the removal of more water in the pores of the cementitious system, the closely-packed polymer particles further coalesce forming a continuous polymer membrane, which binds the cement hydrates together. Thus, a co-matrix of the polymer phase interpenetrating through cement hydrate phase is also being formed.

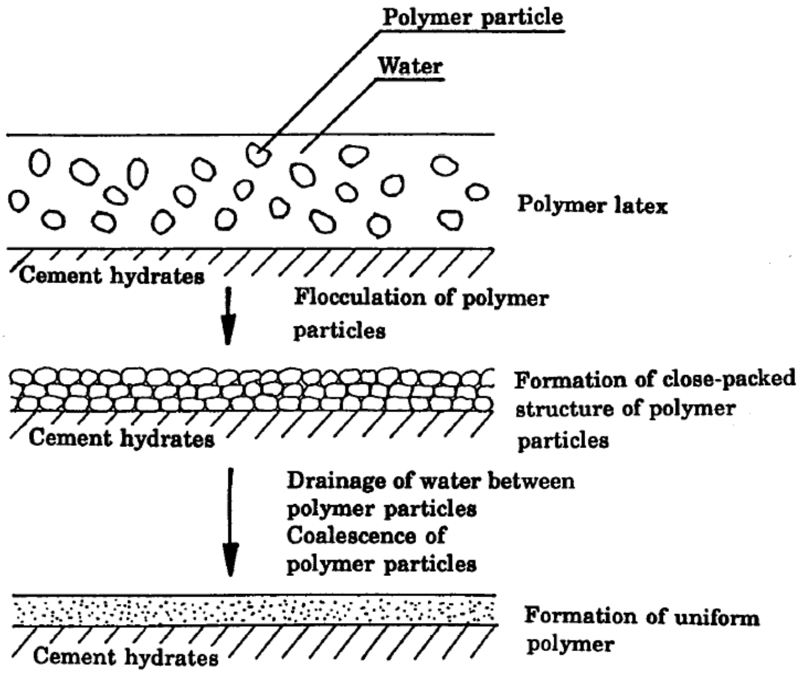


Figure 2.1: Model of the formation of polymer films in a cementitious system (Ohama 1995)

Ohama’s model assumes that the polymer gets uniformly dispersed in the medium and a p/c of not less than 5 % is required for the above polymer mechanism, as discussed earlier. This limitation on dosage may not be valid for all cases of the polymeric systems. Thus, there is a need to consider models that accommodate the differences in the mechanisms of polymer types and the rate of dispersion in the cementitious medium. A model was proposed by Tian et al. (2013) considering the key features of polymer interaction with the cementitious systems; the main aspects of which are explained below.

(i) Initially, when cement, sand, water, and polymer particles are mixed together, no physical or chemical interaction occurs between the constituents of the mix, as shown in Figure 2.2.

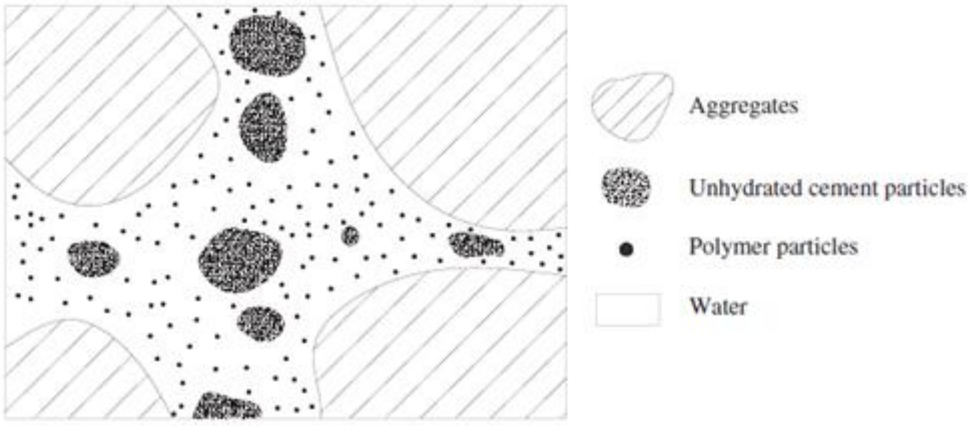


Figure 2.2: Initial distribution of polymer particles in the mixture (Ohama 1995)

(ii) As water and cement come into contact, hydration occurs, releasing calcium ions and hydrated products in the pore solution. Due to chemical bonding and electrical attraction, the polymer particles stick to cement hydrates and the calcium ions in the pore solution, leading to polymer flocculation. A very small part of the polymers also gets adsorbed on the sand particles by physical adherence. If a higher polymer dosage is used, some polymer particles are released freely into the pore solution, which may get trapped by the hydrate or polymer flocculation or sand. Thus, there occurs a localization of polymer modification on the hydrates, cross-linked groups and sand as seen in Figure 2.3.

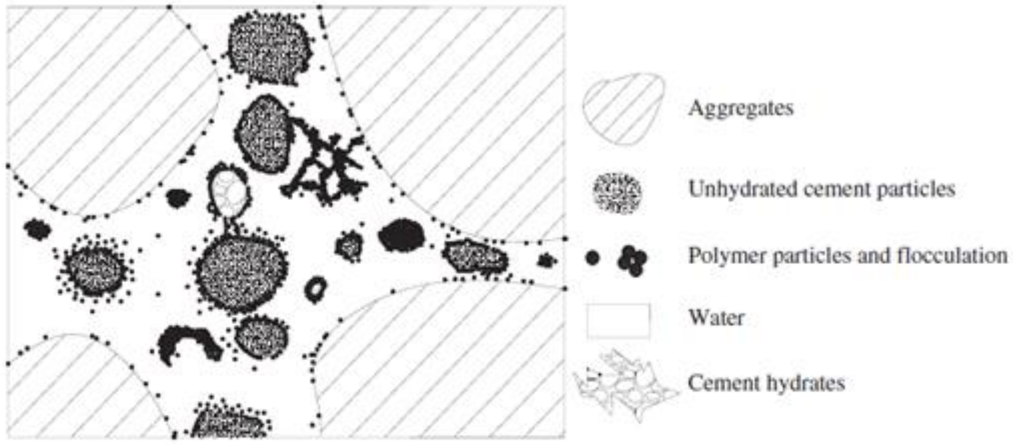


Figure 2.3: Adsorption and flocculation of polymer particles in the mixture (Ohama 1995)

(iii) Polymer particles that entrap the cement and retard hydration process, through the hydration products formed, break through the polymer envelope developed. Hydration products begin to grow in the flocculated polymer; and with more pore solution being used up, the polymer particles come together coalescing into a film, as seen in Figure 2.4.

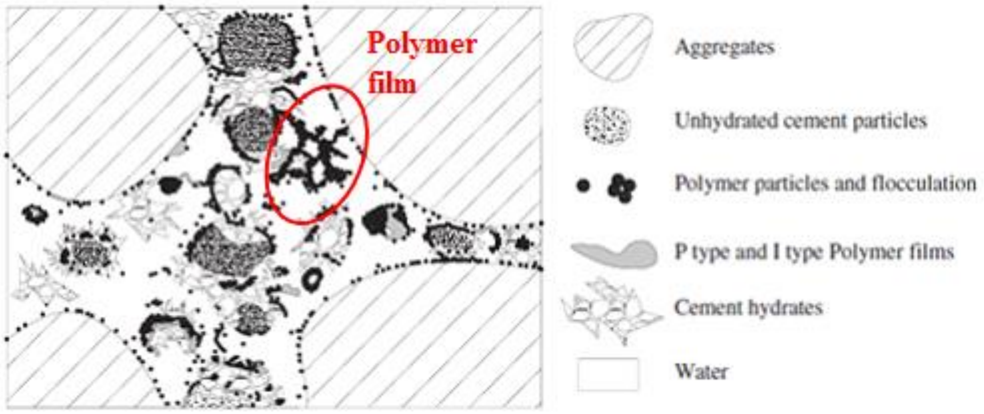


Figure 2.4: Progress of cement hydration and initial formation of polymer films (Ohama 1995)

(iv) In the final stage, processes of hydration and polymer film formation would be almost complete. However, various types of polymer-cement interaction products are formed within the same system, as shown in Figure 2.5.

- Polymer particles adsorbed on the cement grains combine chemically with the hydrates (designated as C type polymer-cement compound).
- Polymer particles linked with Ca $^{2+}$ ions form impure films (designated as I type polymer films).
- Unreacted polymer particles will coalesce to form pure films (designated as P type polymer films). These films and cement hydrates may interpenetrate forming compounds (designated as P type polymer-cement compounds).

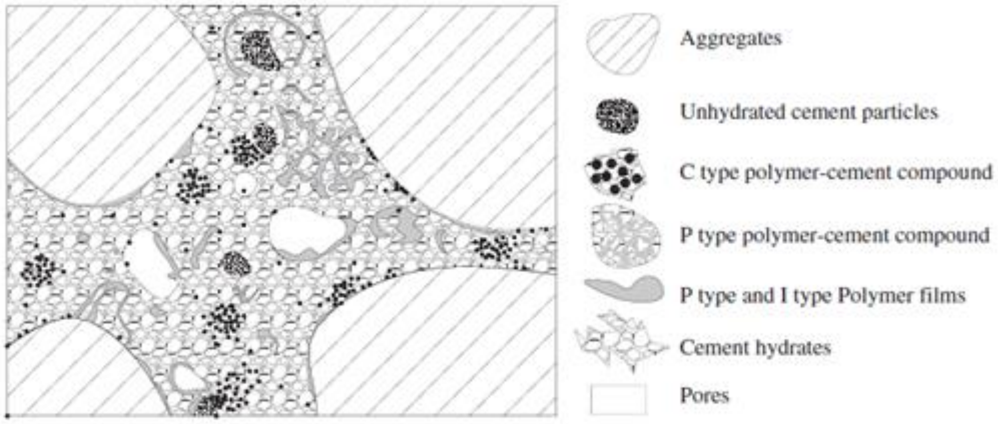


Figure 2.5: Final microstructure formation in polymer modified mortar (Ohama 1995)

This model shows that polymer modifications are not confined to film formation, and various morphologies of compounds are also formed by the interaction of polymers with the cementitious system. The pore refinement of PMMs can be attributed to the film formation in addition to the cement hydration, and other benefits of increased toughness and good adhesion in the system can be attributed to the different hydration-polymer interaction compounds formed. It is also reported that the interaction products formed by the polymer with the cementitious system and hydration products, do not necessarily contribute to the strength development (Tabor 1987). The polymers and polymer film formed at the aggregate-cementitious matrix and in the pores, contribute to the strength of the system (Su 1991). Thus, the actual principle of polymer film formation, accounting for the facts of the localization of polymer film formation in the cementitious system, is well addressed in this model.

2.5 Influence of polymer modification in a cementitious mortar system

The properties of PMMs in terms of strength and durability characteristics differ widely from that of an UCM depending on the several factors. Some of the factors are the polymer to cement ratio, w/c ratio, sand to cement ratio, curing conditions, age and other additives used in the system. In an ordinary portland cement mortar-system, where the hydrated cement matrix and aggregates are bound by weak van der Waals force, the formation and propagation of micro-cracks are facilitated through the interfacial transition zone. In the case of a polymer modified system, the polymer film formed is expected to bridge the micro-cracks formed (Ohama 1995). Also, as discussed, the chemical interaction between the polymer particles and the cementitious ingredients create a better bond in the mortar system as shown in Figure 2.6.

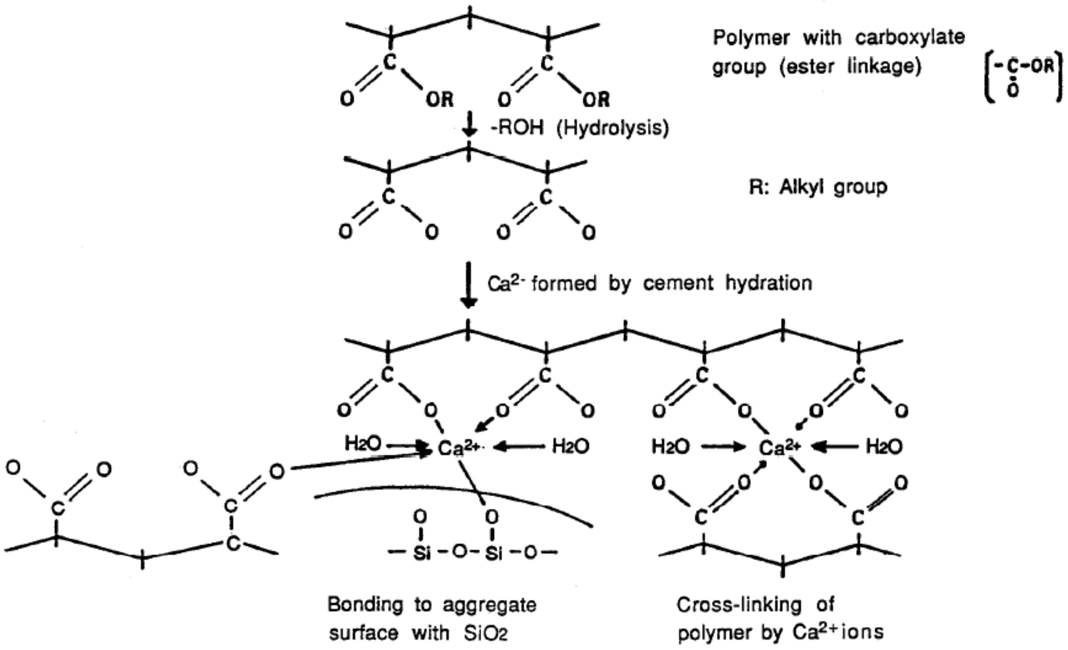


Figure 2.6: Chemical interaction of polymer particles with the cement hydrates and aggregates (Ohama 1995)

The microstructure of the interfacial transition zone (ITZ) was also reported to be influenced by the addition of water soluble polymers. With the incorporation of polymers, calcium ions present in the system get cross-linked with the polymer. This reduces the amount of the calcium hydroxide content and generally creates a coating on the aggregates, thereby reducing the ITZ zone thickness (Kim and Robertson 1998).

For cement mortars modified with SBR latex, at early age (i.e., 7 days), the compressive strength and permeability were adversely affected with polymer addition; and at later ages (i.e., 28 days), the properties improved. This clearly indicates that age is an important factor in the evaluation of the performance of PMMs. Also, the leaching that occurs with curing influences the polymer cement interaction (Siddiqi et al. 2013; Soni and Joshi 2014). It was also reported that a hot dry curing environment provides improved strength and reduced permeability, diffusion and shrinkage to polymeric systems, when compared with conventional cement mortars (Hassan et al. 2010).

2.5.1 Influence of polymer modifications on the fresh properties of cementitious systems

The incorporation of polymers leads to certain modifications of the fresh properties of the mortar, each of which is discussed below.

2.5.1.1 Workability: PMMs can have higher workability compared to UCM even at a lower w/c ratio. The increase in fluidity with PMMs is attributed to the combination of fluidification by the polymer particles and entrained air, and the dispersing action of surfactants employed in the latexes. The increase in air entrainment associated with PMMs is due to the action of surfactants provided in the latexes to avoid re-emulsification and for the stability of the latexes. It is possible that higher entrainment of air leads to formation of larger voids resulting in lower compressive strength (Negim et al. 2015).

2.5.1.2 Water retention: The sealing effect due to the impermeable polymer film formed in PMMs, together with the hydrophilic nature of the colloidal polymer particles themselves, provide higher water retention to PMMs. The water retention increases with an increase in polymer ratio, and finally stabilises at a certain concentration for each polymer type. This property of PMMs makes them an excellent choice for direct bonding over water-absorbing substrates, like dry cement mortars and ceramics (Wang and Wang 2011).

2.5.1.3 Bleeding and segregation: Though PMMs attain better flow than UCM, they have an excellent resistance to bleeding and segregation. This is on account of the hydrophilic nature of the colloidal polymer particles, in combination with the water reducing nature of surfactants present in the latexes. The addition of polymers also increases the cohesion between the aggregates and cement matrix, which helps in reducing segregation (Hayakawa and Soshiroda 1986; Lubetkin 1987).

2.5.1.4 Setting time: One setback faced with the polymeric addition in the cementitious system is the delay in the setting time, which increases with an increase in polymer dosage. This is due to the retardation of cement hydration by some surfactants, such as alkylbenzene sulfonates and caseinates, that get adsorbed on the binder surface (Beeldens 2002).

2.5.2 Influence of polymer modifications on the hardened properties of cement systems

All applications of polymer modified mortars require a moderate compressive strength and flexibility. Polymeric addition to cementitious systems affects both compressive and flexural strength with the latter benefiting from a more positive impact than the former.

2.5.2.1 Compressive strength

The compressive strength of mortar is found to depend on the gel space ratio, which is the ratio of the volume occupied by the hydrated products to the sum of the volumes of the hydrated products and capillary pores. For an ordinary portland cement concrete, the compressive strength is related to its gel space ratio as follows (Neville 1996).

$f_{cr} = 234\ r^3$ MPa……………………………………………………………Eq. (2.1)

where,

f_{cr} = compressive strength of the concrete, MPa

r = gel space ratio of the mix and is given as,

$r = \frac{k_h\, v_c\, \alpha}{v_c\, \alpha + w/c}$ ……………………………………………………Eq. (2.2)

where,

k_h = hydrate volume expansion factor for ordinary portland cement, which indicates the volume of hydrates generated when unit volume of cement is completely hydrated

v_c = specific volume of cement with the value 0.317 cm^3/g, and

α = degree of hydration of cement.

Eqs. 2.1 and 2.2 hold good for UCMs. However, in a PMM system, with the polymer being a relatively softer material than the cement hydrate and aggregates, it can be considered more as a space or void in the cementitious system. Therefore, the gel space ratio of a polymer modified mortar system can be given as (Ma & Li 2013),

$r = \frac{k_h\, v_c\, \alpha}{v_c\, \alpha + \frac{w}{c} + \eta\, (\frac{p}{d})}$……………………………………………………Eq. (2.3)

where,

p = polymer to cement ratio

d = polymer density, and

η = effectiveness coefficient, which signifies extent to which the polymer can be considered as space. For example, η = 0 means the polymer is considered as an aggregate and $\eta = 1$ means the polymer is considered completely as space (i.e., void). The η-value assigned to a polymer depends on its type and rigidity.

From Eq. 2.3, with higher dosages of polymer being used, lower will be the gel-space ratio and hence, lower will be the compressive strength, and the extent of decrease depends on the polymer type and rigidity. On the contrary, studies have also shown an increase in gel space ratio with increasing dosages of polymer due to polymers decreasing the total water requirement of the binder and hence, lowering porosity (Heikal et al. 2001). Therefore, the reduction in compressive strength can be kept lower by using a less stiff polymer that is closely-packed and providing an appropriate curing condition that yields a higher k_h-value. It was reported that the decrease in compressive strength is more when the curing period is inadequate (Fun et al. 2015). The gel-space ratio is found to increase with extended curing periods due to the increase in the amount of hydration products formed.

Aggarwal et al. (2007) reported that the compressive strength of PMMs were lower than that of the UCM when higher dosages of polymer (20 % by weight of cement) were used. For p/c less than 10 %, though the absolute strength was lower than UCM, the strength was found to improve with age. This is due to the fact that, in an UCM, the hydration process will be nearly complete by 28 days, while in a polymer modified mortar, the polymer interaction can extend to about 90 days after the hydration process, without the need of any external curing. Thus, by modifying with a suitable dosage of polymer and curing, the desired properties of PMMs can be attained to meet the functionality. Also, the usage of other cementitious materials like silica fume in conjunction with polymers can help overcome the effects of loss in compressive strength of mortars compared to direct substitution with polymers (Gao et al. 2002).

2.5.2.2 Flexural strength

Polymer addition in any cementitious system has greater influence on the flexural strength than any other mechanical properties. Studies by Schorn and Schiekel (2001) revealed that a wet period followed by dry curing results in higher flexural strength. This type of curing ensures a continuous polymer film formation along with cement hydration due to the polymer particles being available in pore solution. If the dry curing precedes the period of wet curing, polymer film formation will start sooner, simultaneously with hydration. This will result in encapsulation of cement hydrates by polymer products precipitating a polymer phase. In some conditions, an effective polymer film formation may not occur uniformly; nevertheless, even in such a state the addition of polymer can limit the formation of micro-cracks and delay the propagation when loaded (Knapen and Gemert 2015). The constituents of the mortar would be effectively bind by the polymer film resulting in a higher flexural strength. However, the degree of enhancement in strength depends on the type of polymer, dosage and effectiveness of binding matrix formed. Hence, it is necessary to study the adsorption rate of polymers at various dosages which would render better usage of PMMs.

2.5.3 Influence of polymer modifications on durability of cementitious systems

Various studies have been done on the influence of polymeric additions on the durability properties of cementitious systems. It was found that polymeric addition can enhance durability in terms of resistance to water permeability, carbonation and chloride penetration (Kwan et al. 2015). Studies by Nepomuceno and Andrade (2006) have reported that the enhanced durability is due to the increased workability at lower water-binder ratio and lower ionic concentration of chemical composition in the cement pore solution, leading to lower porosity and higher resistivity.

2.5.3.1 Chloride ingress

The chloride ion penetration depth and apparent chloride ion diffusion coefficient of the PMMs were found to be lower than that of UCMs (Ohama et al. 1987). The increased chloride penetration resistance of PMMs is attributed to the interaction of polymer particles with hydration products (Yang et al. 2009). Tri-calcium aluminate (C_3A) phase of cement is readily soluble in water and reacts with gypsum to form ettringite (Af_t). Ettringite reacts further with C_3A forming monosulphate phase (Af_m). With polymeric additions, C_3A phases are entrapped in the cement grains reducing the access to ettringite for reaction. Thus, polymeric addition encourages the reaction of

C_3A with gypsum leading to the formation of stable ettringite. The Af_t phases formed, get converted to chloro-aluminates due to the substitution of sulfate ions by the chlorides in the calcium sulphoaluminate hydrates. At higher dosage of the polymer content, there will be a higher level of chlorides being bound with the polymers and hence a lower diffusion coefficient for the chlorides. The summary of reactions in PMMs that facilitate higher resistance to the ingress of chlorides is given below.

$CaO.Al_2O_3$ (C_3A) + 3 $CaSO_4$.$2H_2O$ (gypsum) + 32 H_2O → $CaO.Al_2O_3$.$3CaSO_4$.32 H_2O (Af_t))……..Eq. (2.4)

$3CaO.Al_2O_3$ + $3CaO.Al_2O_3$.$3CaSO_4$.$32H_2O$ (C_3A) → 2($3CaO.Al_2O_3$.$3CaSO_4$.$12H_2O$) (Af_m) + $CaSO_4$ + $8H_2O$……..………...Eq. (2.5)

3 $CaO.Al_2O_3$ .3 $CaSO_4$.32 H_2O (Af_m) + 6 Cl^- → 3CaO. Al_2O_3. $3CaCl_2$. 32 H_2O (chloride binding) + $3SO_4^{2-}$……..Eq. (2.6)

2.5.3.2 Corrosion protection

Polymeric mortars are found to have significant applications in the corrosion protection of embedded steel. Polymeric additions help maintain the alkalinity of the system and protect the passive oxide layer on the steel reinforcement bars (Hawary et al. 2004). Also, the PMMs have excellent bonding with the reinforcement systems.

2.5.3.3 Resistance to environmental actions

For most polymers, a small amount of carboxylic acid is chemically bound on the surface, which ionizes in the alkaline environment and reacts with the Ca^{2+} ions. The chemical bonding of the polymers with Ca^{2+} ions provides a better stability for the polymer latexes and improved adhesion with the substrate. Cement grains interact with the polymeric particles having calcium ions, and this reduces the formation of calcium hydroxide (Afridi et al. 1989). At higher p/c ratios, where the polymer is more uniformly dispersed, the pore structure was found to be more compact. The reduced pore size in PMMs lowers the ingress of CO_2 leading to higher carbonation resistance. From durability studies on polymer modified mortars, the differences in performance after subjecting to extreme treatment conditions, like soaking in erosive solutions (5 % HCl, 5 % H_2SO_4 and 5 % NaOH), freeze-thaw cyclic treatment and drying-wetting cycles, were identified to depend on the nature of the polymer film formed, each of which enhanced the properties of the mortar in different ways (Wang and Zhang 2015).

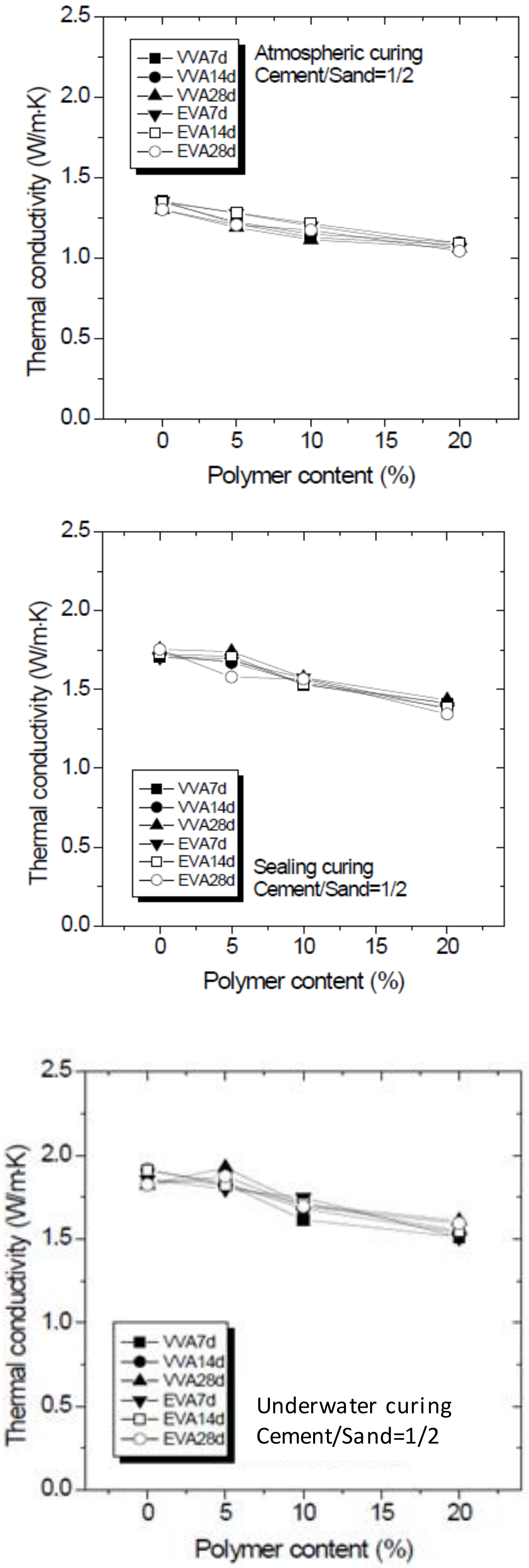


Figure 2.7: Influence of moisture content on the thermal conductivity of PMMs (i) air curing (ii) sealant curing (iii) underwater curing (Noguchi et al. 2016)

However, it is necessary to acknowledge the fact that the durability of polymeric systems depends on the exposure conditions. Noguchi et al. (2016), identified variations in thermal conductivity for PMMs subjected to various curing types and hence moisture contents (atmospheric, sealing, under water curing). An increase in moisture content can result in higher thermal conductivity, as shown in Figure 2.7. The thermal conductivity was seen to progressively decrease as the curing type was changed from atmospheric to sealed to under water curing. Other studies have also reported that in the presence of sulphur dioxide and oxygen, ultraviolet radiation is found to improve cross-linking in polymers (Fried 2003; Mills 1993), and the equal susceptibility to moisture especially in the form of dew (Springer 1984), makes its applications difficult in some conditions.

2.6 Performance evaluation of PMMs at elevated temperature conditions

2.6.1 Microstructural degradation of PMMs at elevated temperature conditions

Crystalline polymers have an ordered network of polymer chains whereas amorphous polymers have disordered network system. The former is characterized by a melting point and the latter by a glass transition temperature. As the melt of polymer is cooled, its viscosity increases. If the polymer is not able to crystallise during the cooling regime, and the temperature is further lowered, polymer becomes glassy. Any further reduction in temperature makes it an elastic polymer glass. This temperature at which it transforms from a rigid state to a glassy state is called as its glass transition temperature. Polymer molecules, below its glass transition temperature (T_g), exist in an amorphous state with no regular repeating pattern of polymeric chains. At this stage, the polymer chains do not have enough energy to move around (Young and Lovell 2011). When the polymeric systems are exposed to elevated temperatures, polymeric chains get delinked causing them to move, and above a certain temperature, the change from the amorphous to a more ordered arrangement occurs. The strengthening of the polymer films seen at higher temperature is mainly attributed due to this change of polymeric state.

There are several factors on which the glass transition temperature of polymers depends, the most important of which are being listed below (Young and Lovell 2011):

(i) The lower the rate of cooling, the lower will be the glass transition temperature.

(ii) Polymers with more flexible chains possess a lower value of glass transition temperature.

(iii) Presence of side groups and higher molar mass restricts rotation and increases the glass transition temperature.

The heat capacity is found to increase with an increase in the glass transition temperature resulting in a drastic loss in the mechanical properties.

Most of the polymers that are widely used for cementitious materials have their glass transition temperature between 100 °C to 150 °C, beyond which the properties can be detrimental. Systems with polymeric latexes seem to experience a greater reduction in strength when the temperature is above the corresponding T_g of the polymer (Ohama 1995).

Microstructural degradation of the polymeric state in PMMs subjected to heating are generally studied using techniques of Thermo-Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). The heat flow plotted along the ordinate of the graph plotted in Figure 2.8 is a measure of the heat absorbed or released by the polymer due to its thermal transitions. As discussed above, when the polymers reach T_g, the heat capacity is found to increase, and this is shown as a rise in the plot of heat flow versus temperature in a DSC plot. Upon crystallisation, polymers having gained sufficient energy, would give out heat indicated as a drop in the plot. Thus, the phase changes in polymer at elevated temperatures can be characterised using DSC.

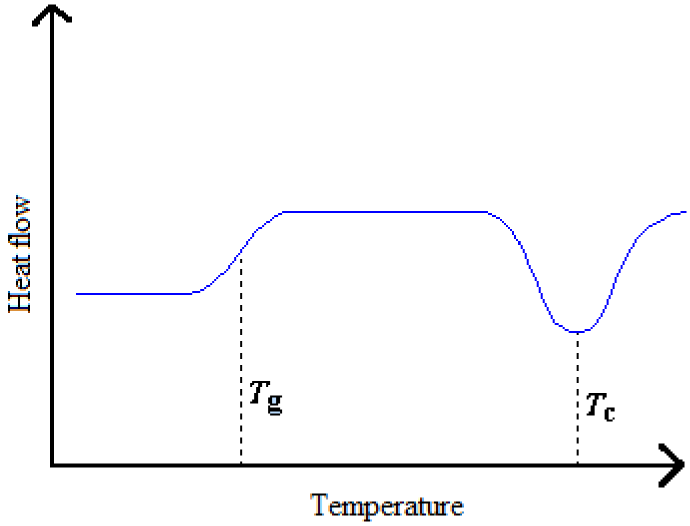


Figure 2.8: Plot of heat flow versus temperature in DSC for a polymeric material

At normal conditions, the amount of calcium hydroxide (CH) formed in PMMs is less than that formed in UCMs due to the adsorption of CH by the polymer films (Almeida and Sichieri 2006; Benosman et al. 2012). With elevated temperature, there is the formation of additional calcium silicate hydrate (C-S-H) from the anhydrous clinker phases resulting in an increase in portlandite (CH). In addition, the deterioration of the polymer film above a certain elevated temperature (depending on the polymer type) also releases CH into the system. Hence, the CH intensity increases at elevated temperature in PMMs than UCM. At elevated temperature, the calcium carbonate intensity was also found to be more in PMMs than in UCM, which can be attributed to the partial carbonation of CH (Yang et al., 2009).

2.6.2 Factors influencing the performance of PMMs at elevated temperatures

The performance of PMMs at elevated temperature is controlled by the nature of the polymer (functional group), glass transition temperature, dosage, curing conditions, age of exposure, and testing parameters (rate of heating and duration of exposure).

2.6.2.1 Influence of polymer type, dosage and curing

In PMM, the effectiveness of polymer modification in the cementitious system controls the performance at various exposure conditions. A short duration of moist curing up to seven days ensures early commencement of polymer film formation (after the wet curing) along with the hydration (Ramli et al. 2013). Therefore, the performance of PMMs is better with systems subjected to a short curing regime with less of hydration products formed to deteriorate at higher temperature conditions. On the other hand, extended curing (i.e., 28 days) results in a fully developed C-S-H system that deteriorates at elevated temperatures, hampering the integrity of the system.

From the studies done by Muthadhi and Kothandaraman (2014) on the effect of elevated temperature on the performance of PMMs, a marginal increase in compressive strength was reported even at an exposed temperature of 200 °C and 400 °C, beyond which a loss in strength was noted up to 800 °C. The reason for the initial increase in compressive strength can be attributed to the further hydration of the unhydrated cement particles, which occurs at higher temperatures. There could be a fall in strength when the temperature is more than 300 °C due to the deterioration of the polymeric films resulting in internal stresses and micro cracks.

From Figure 2.9, with UCM (0 % p/c) and PMMs (up to 10 % p/c), an initial increase in strength was noted beyond there is a drop in strength. For PMMs with p/c greater than 10 %, a decrease in strength was noted with the initial increase in temperature (200 °C), thereby indicating that polymeric additions play a significant role in influencing the properties of cementitious systems at elevated temperatures. Hence, polymer content greater than 10 % is detrimental elevated temperatures.

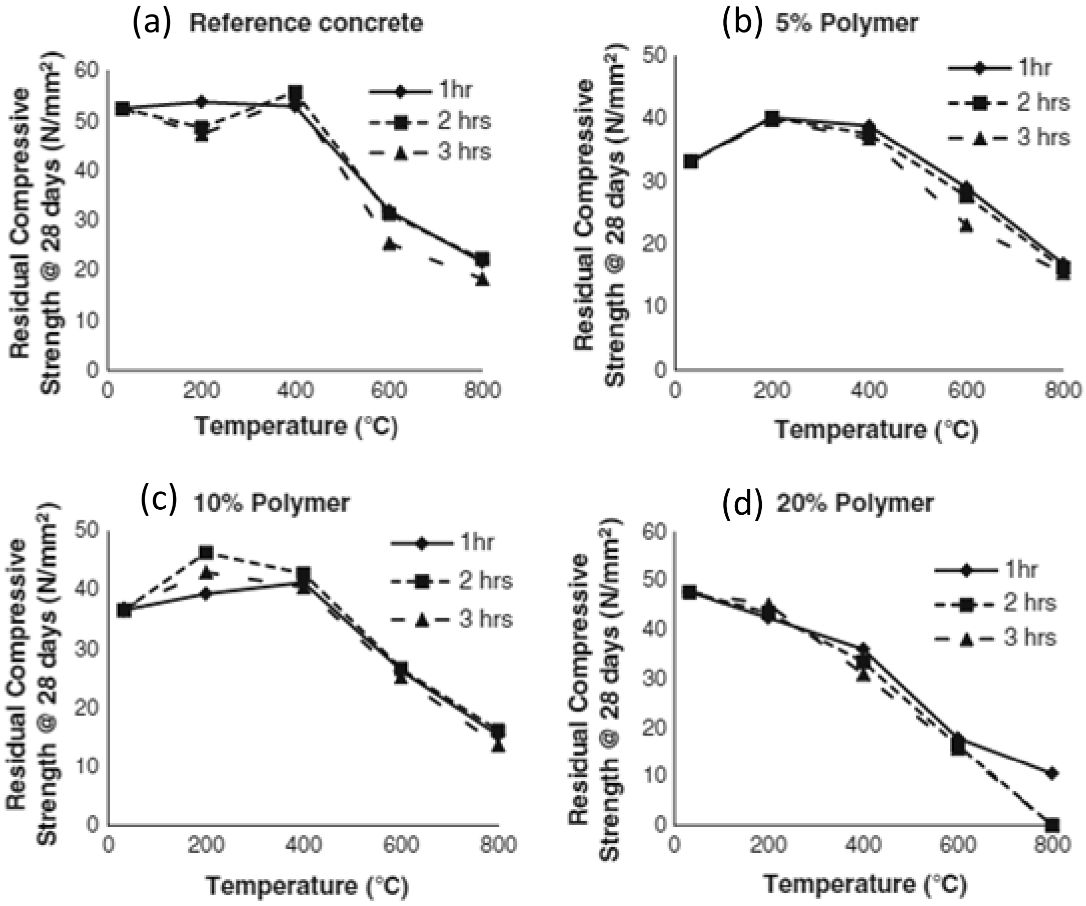


Figure 2.9: Trend of compressive strength at different dosages of PMMs at various exposure temperature (Muthadhi and Kothandaraman 2014)

Apart from strength, properties such as thermal conductivity were also reported to be altered at conditions of elevated temperature. Thermal conductivity of the PMMs improves with exposure to temperature due to increased porosity (Ribeiro et al. 2003; Noguchi et al. 2016). Polymers being good insulators, at higher dosages, lower the thermal conductivity of the system. It has been reported that polymer modified systems employing lower p/c (i.e., <0.15) have heat and fire resistance equal to that of an unmodified mortar (Ohama 1995).

2.6.2.2 Influence of elevated temperatures and heating rate

From the studies mentioned in the previous sections, it is understood that the glass transition temperature influences the performance of PMMs. It has been reported that the flexural strength of most latex modified mortars at 100 °C tends to reach a maximum value because of the strengthening of polymer films on drying (Ohama 1995). However, when heated to 150 or 200 °C, the strength is found to decrease within a short period of time. The thermal transitions of the polymer that occur at various temperatures, directly impact the response of PMMs when exposed to such temperature conditions. It has also been established that the thermomechanical properties of composites depend not only on temperature but also the heating rate and duration (Dimitrienko 1996). Higher the heating rate and longer the duration, faster is the deterioration of the polymeric cementitious systems.

2.7 Performance evaluation of PMMs under fire conditions

Cement mortar and concrete are relatively inert under fire conditions but the incorporation of polymers into the cementitious system may reduce the fire resistance, which will lead to loss of safety for the intended application. The general properties tested at fire conditions for PMMs are the combustibility, which is evaluated based on the time until smoking and flaming. However, the evident damage for most civil structures when exposed to fire is mainly the spalling of concrete, which occurs due to the rise in the water vapour pressure in combination with the generation of flammable gases. For any mortar, spalling occurs at heating rates exceeding 3 °C/min (Khoury 2000), lower w/c ratios and low gas permeability (Phan et al. 1996). The density of concrete has a major impact on explosive spalling (Hertz 2003), which is more at higher compressive stresses of concrete (Terassi et al. 2012).

When PMMs are evaluated for their performance at fire conditions, it has been seen that for more than 10 % dosage of polymer, spalling was reduced for the polymeric systems as they had enough voids for vapour evacuation that caused the release of steam pressure (Han et al. 2011).

Generally, fires can be classified as open and closed fires, the latter being severe for its sudden rate of temperature rise. Fire in confined areas such as tunnels represent closed fires, where it is difficult to extinguish the fire and evacuate people. Such fire breakouts are well represented by the RABT curve (German fire curve), where the temperature rises rapidly to 1200 °C in 5 minutes, is maintained for an hour and reduced to 15 °C in 110 minutes. This curve could be used to assess materials used as tunnel linings or in such applications, where an outbreak of fire would result in a sudden temperature rise.

Generally, for materials used in construction, assessment of the fire performance is done by subjecting them to heating as per the ISO 834 curve, which has been developed based on the burning rate of normal building materials. The corresponding heating rate shown in Figure 2.10 follows Eq. 2.7.

$T = 20 + 345 (\log(8T+1))$ ....Eq. (2.7)

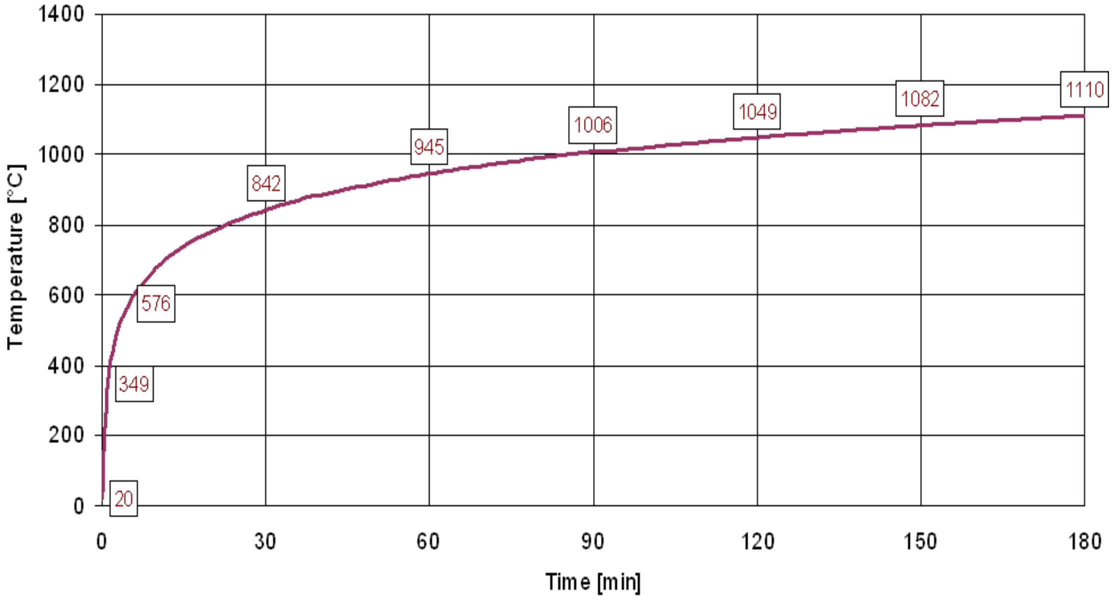


Figure 2.10: ISO 834 curve for building materials

2.7.1 Combustibility of PMMs in a fire

One of the basic requirements expected from any plastering or repair mortar is incombustibility or at least combustibility without any asphyxiation or discomfort to the occupants. A good mortar is expected to release minimal emissions with maximum time elapsed from the point it begins to release fumes to the time it catches fire (Won 2012). In other words, the thermal degradation of the polymers used in the mortars should not result in any additional toxicity.

For polymer modified mortars, the combustibility performance depends on the polymer type and dosage applied. The grading of some commonly used polymeric additions as per JIS A 1321 (Ohama 1995) is given in Table 2.1: Grading of polymeric modified mortars by JIS A 1321.

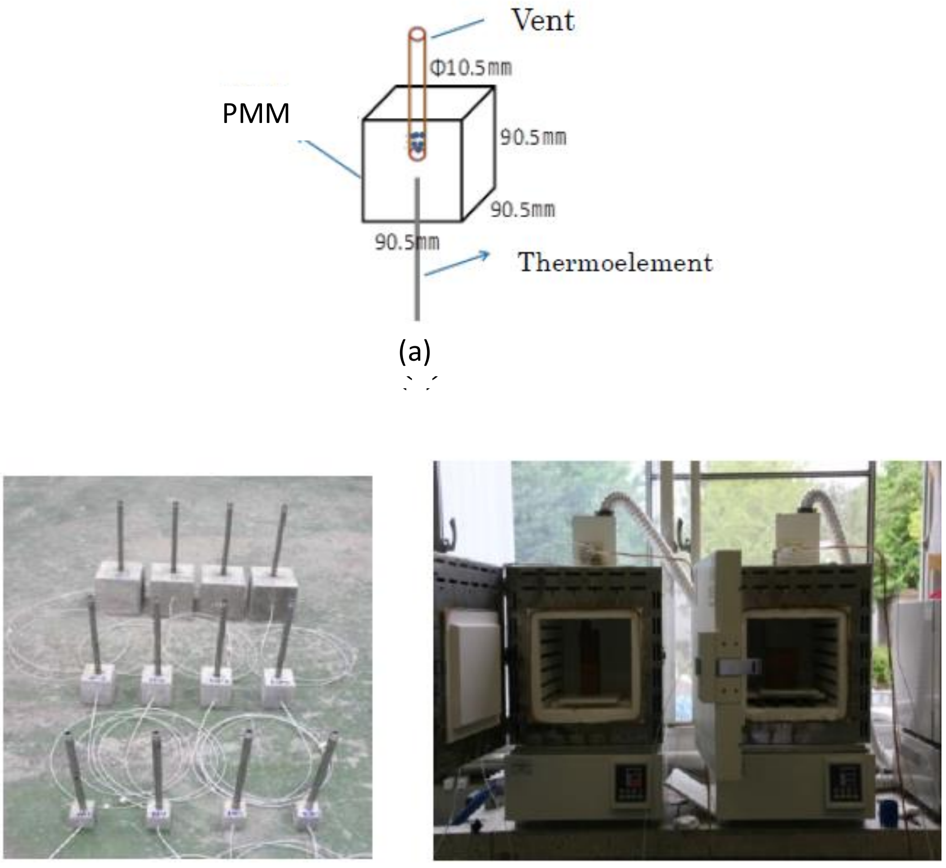
Table 2.1: Grading of polymeric modified mortars by JIS A 1321 (Ohama 1995)

Type of polymer	Polymer to cement ratio (%)	Polymer content (volume %)	Time until smoking (sec)	Time until flaming (sec)	Time to reach 810 ^{o}C (sec)	Class of incombustibility
SBR PMMs	5	2.1	155	89	-	Grade 1
	10	4.22	62	49	290	Grade 2
	15	6.27	52	45	304	Grade 2
	20	8.4	26	26	329	Grade 3
PAE PMMs	5	1.71	No smoke	No flame	-	Grade 1
	10	3.33	128	82	256	Grade 2
	15	4.94	60	35	144	Grade 2
	20	6.45	35	35	80	Grade 3
PVDV PMMs	5	1.37	No smoke	No flamed	-	Grade 1
	10	2.8	No smoke	No flame	-	Grade 1
	15	4.19	No smoke	No flame	-	Grade 1
	20	5.58	No smoke	Noflame	-	Grade 1
PVAC PMMs	5	1.76	Nosmoke	No flame	-	Grade 1
	10	3.56	No smoke	390	-	Grade 1
	15	5.43	No smoke	303	-	Grade 1
	20	6.58	No smoke	60	-	Grade 1
EVA PMMs	5	1.77	No smoke	No flame	-	Grade 1
	10	3.65	99	90	-	Grade 1
	15	5.73	51	44	102	Grade 2
	20	7.51	41	41	220	Grade 2

SBR – styrene butadiene rubber; PAE – poly acrylic ester; PVAC – poly vinyl acetate; PVDC – poly vinyledene chloride; EVA – ethylene vinyl acetate.

2.7.2 Internal gas pressure and spalling of PMMs at fire

Generally, when concrete or mortar is heated, there is a thermal incompatibility between the cement paste and aggregate resulting in internal stresses and micro-cracks that weaken the concrete (Chandra et al. 1980). These stresses can result in explosive spalling and delamination in composite structures when subjected to fire (Feih et al. 2008). As spalling of concrete mainly occurs due to the gases produced at high temperatures and build-up of the internal pressure, it becomes necessary to quantify the gas pressure developed due to a fire. At high temperatures, the polymer in PMMs undergo thermal decomposition causing the release of gases through the pores. The setup for measurement of gas pressure and the results obtained are shown in Figure 2.11 and Figure 2.12, respectively, from Imamoto et al. (2016).



(a)

(b)

Figure 2.11: Setup for the measurement of gas pressure of PMMs: (a) Specimen configuration, and (b) Measuring devices (from Imamoto et al. 2016)

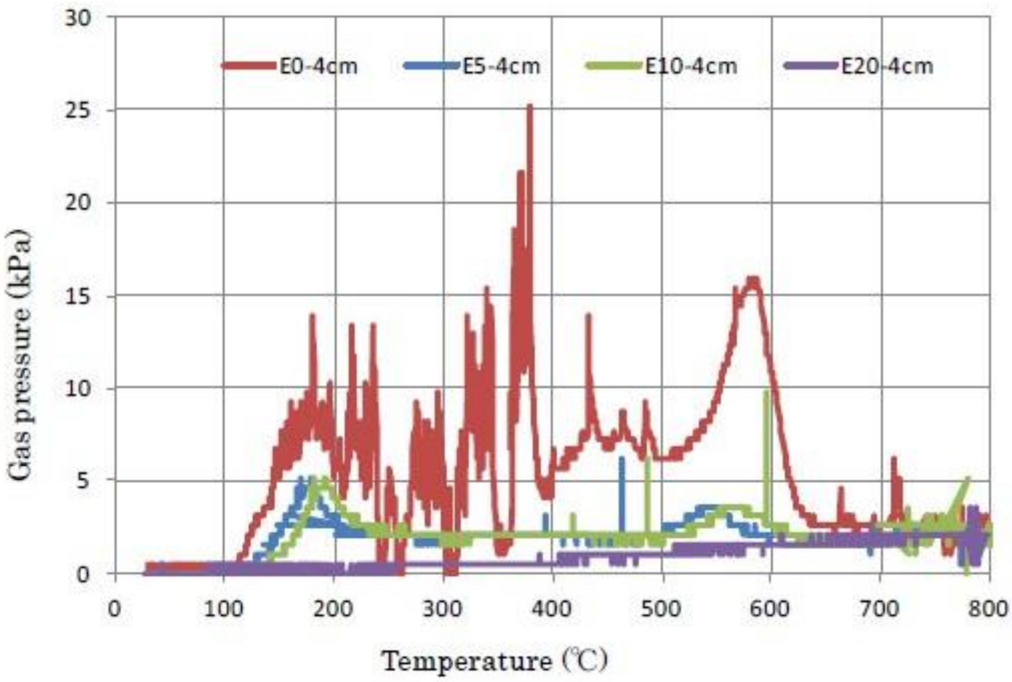


Figure 2.12: Variation of gas pressure with temperature for different dosages of EVA modified mortars (from Imamoto et al. 2016)

From the results, it is inferred that highest maximum gas pressure is developed in the UCM. Further, in the PMMs, the maximum gas pressure developed decreased with an increase in the polymer content. When a p/c of 20 % was employed, the pressure developed was not greater than 5 kPa at any temperature. Thus, the risk of spalling reduced with an increase in polymer content. This was because the PMMs undergo deterioration when heated forming channels through which the gases escape, preventing pressure build-up inside the polymeric systems (Lura and Terrasi 2014).

A simplified method of evaluating the spalling resistance of mortar has been proposed by Hamasaki et al. (2016), where cylindrical specimens of 50 × 100 mm are placed in a furnace and subjected to the heating rate of the required fire curve. The specimen is exposed to temperature up to 800 °C since spalling generally occurs for a temperature range of 600 °C to 800 °C. Based on the appearance of the specimen after exposure to high temperature, represented in Figure 2.13, the stages of spalling are classified as in Table 2.2.

Figure 2.13: Stage 1 to Stage 5 damage of test specimens (left to right) after spalling (from Hamasaki et al. 2016)

Table 2.2: Stages of spalling based on the extent of damage

Stages of spalling	*Damage states*
1	Cracks
2	Peeling of the surface layer only
3	Peeling and spalling of the surface layer only
4	Localized inner spalling
5	Generalized inner spalling

When the appearance of the tested specimen varies from cracks to inner spalling, spalling is considered to have occurred in an alarming state, posing danger to occupants. The temperature ranges, where these visual changes occur must be noted for recommending the critical temperature of exposure for spalling.

2.8 Summary

PMMs are used in various applications such as water proofing, repair mortars, and overlays on floors and pavements. The interaction of polymers with cementitious system results in pore refinement with difference in morphologies of polymer hydration interaction products. This enables the PMMs to have better workability, flexibility, bond strength and resistance to external ingress. An appropriate combination of dosage and curing type is the prime factor on which the polymer film formation depends and hence, its performance. A short period of wet curing (i.e., less than 7days) followed by dry curing is found to favour the mechanism of polymer film formation subjective to the polymer type, dosage, and exposure conditions.

Polymer addition is found to positively impact the fresh and hardened properties, except for the air entrainment and compressive strength. However, the retention of properties of the PMMs at various temperature conditions should be considered with caution, as every polymer system has a critical temperature, beyond which sudden shift or changes in properties are expected to occur.

CHAPTER 3

EXPERIMENTAL PROGRAMME AND METHODOLOGY

3.1 Introduction

The experimental programme for the study is set to evaluate the performance of polymer modified mortars at various conditions of testing, namely at normal conditions; after exposure to accelerated conditions of weathering, elevated temperatures and fire conditions. The mortars were tested for the engineering properties (compressive strength and flexural strength), transport properties (water permeability) and shrinkage, along with the microstructural features being analysed at these exposure conditions. The common application of PMMs being repair, waterproofing and plastering, it is expected to meet compressive and flexural strength requirements. PMMs are preferred over ordinary mortars owing to improved durability features for which the water permeability and shrinkage properties of the mortars were included in the study, and microstructural analysis were carried out to validate the performance drifts at various curing and exposure conditions. Microstructural studies on the polymeric systems were done using techniques of SEM, X-Ray Diffraction (XRD) and Mercury Intrusion Porosimetry (MIP) to understand the compositional and morphological specifics and deterioration of the compounds in mortars at various exposure conditions.

This chapter presents details of the materials used for fabrication of mortars, the curing and exposure conditions adopted, and the experimental techniques adopted for the evaluation of polymeric mortars.

3.2 Materials used

This section discusses the materials used for preparing mortars with properties and specifications they conform to.

3.2.1 Cement

Ordinary portland cement (OPC) of 53 Grade conforming to IS: 12269 – 1987 (reaffirmed 2004) was used in this work. The physical and chemical properties of the cement are shown in Table 3.1 and Table3.2, respectively.

Table 3.1: Physical properties of OPC 53 Grade cement used

Test	Result	Limit (IS: 12269)
Total chloride (as Cl) % by mass	0.02	< 0.05
Magnesia (as MgO) % by mass	1.96	< 6
Sulphuric Anhydride (as SO_3), % by mass	2.25	< 2.5
Ratio of % of alumina to that of iron oxide	0.87	>0.66
Sodium oxide (as Na_2O), %	0.07	< 0.6
Potassium oxide (as K_2O), %	0.48	-

Data provided by the National Test House (Southern Region); Method(s) used for test is IS: 4032 - 1985 (reaffirmed 2005)

Table3.2: Chemical properties of OPC 53 Grade cement used

Properties tested	Code followed	Test result
Standard consistency	IS: 4031 Part 4 – 1988	28 % by weight of cement
Initial and final setting time	IS: 4031 Part 5 – 1988	Initial setting time: 265 min. Final setting time: 330 min.

3.2.2 Fine aggregate (sand)

The aggregate used in this study was locally available river sand, passing through sieve of 4.75 mm opening, with the grain size distribution as shown in Figure 3.1. Physical properties of the sand are tabulated in Table3.3.

Table3.3: Properties of fine aggregates used

Properties tested	Code followed	Test result
Specific gravity	IS 2386 (Part III) -1963 reaffirmed 2002	2.79
Water absorption	IS: 2386 (Part 3) -1963 reaffirmed 2002	3.18 %
Fineness modulus	IS:2386 (Part 1) – 1963	3.11

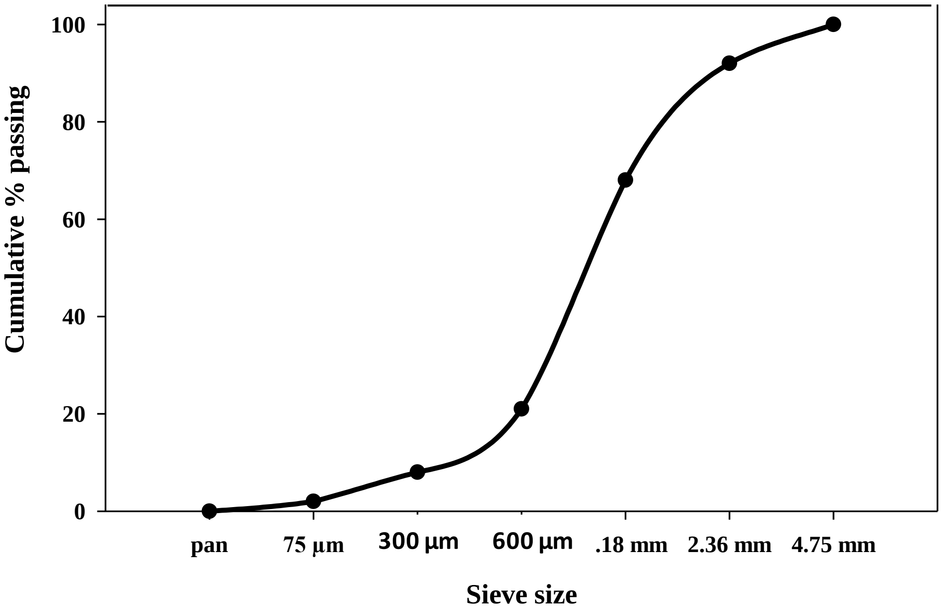


Figure 3.1: Grain size distribution of fine aggregates

3.2.3 Polymer latexes as integral admixtures

In this study, Styrene butadiene rubber (SBR), poly acrylic ester (PAE) latex and silane modified polymeric emulsion (SIL) systems were used as additives to modify the mortar. SBR and PAE polymers have been commonly used for integral waterproofing system in past decades. Silanes, on the other hand, are commonly used as coupling and cross-linking agents to couple organic polymers to inorganic materials. In this study, a silane modified emulsion polymer is used as an integral additive in the cementitious mortar to investigate its potential; for this product, the manufacturer has indicated that the silane has been processed with an organic backbone of mostly alkyd groups and water to form the emulsion. The solid content in the polymer latexes and emulsions were determined as per ASTM C494. FTIR analysis was also done on the polymers studied in the liquid state. Details of each of the polymers related to the interaction in the cementitious system are discussed in the next section.

3.2.3.1 Styrene butadiene rubber polymer (SBR) latex

The SBR consists of two monomers – styrene and butan-1,3-diene whose emulsion polymerisation is initiated by free radicals. The final product is a well cross-linked polymer system with good abrasion resistance and aging stability when used with additives. Molecular structure of SBR consists of both flexible butadiene chains and rigid styrene chains, which provides good mechanical properties, water tightness and abrasion resistance when an appropriate polymer to cement ratio is used (Soni and Joshi 2014). The basic polymeric structure of SBR is given in Figure 3.2.

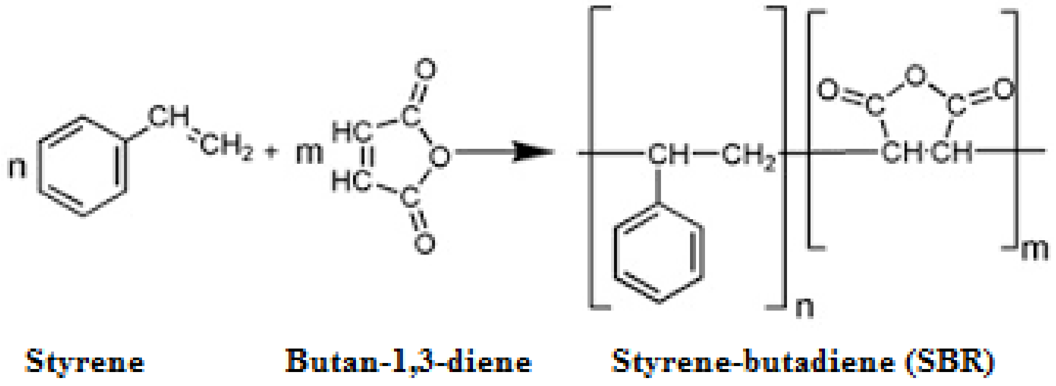


Figure 3.2: Chemical structure of SBR polymer latex (Ohama 1995)

The SBR latex used for the study, with a solid content of 44%, was added in p/c dosages of 4.5 % (as recommended by the manufacturer) and 10 % (suggested in the literature as the minimum for effective polymer film formation. FTIR analysis was done on the polymer latexes in the liquid state using a Spectrum One FTIR Perkin Elmer Spectrometer, where the molecular vibrations were used to identify compounds. The FTIR spectrometer used could scan the mid infra region in the range of 450 to 4000 cm^{-1} with a resolution of 1 cm^{-1}. The FTIR analysis plot of SBR latex is shown in Figure 3.3. The peak at 1651 cm^{-1} indicate the presence of an aromatic ring with a diene, and the peak at 700 cm^{-1} reflect the presence of cis-butadiene. The C=CH2 group is indicated by the peak at 968 cm^{-1} (Kuptsov and Zhizhin, 1998).

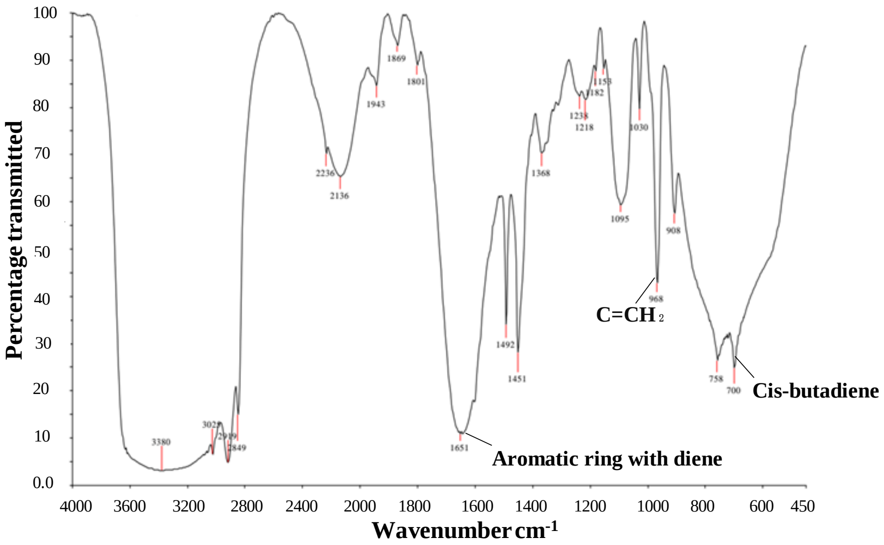


Figure 3.3: FTIR analysis of SBR polymer latex

As discussed in the mechanism of polymer film formation in Section 2.4, as hydration advances and water content within the system reduces, the polymer particles coalesce forming an interconnected polymer network within the cementitious system. This network of polymer increases the durability of the system by blocking pores and bridging the microcracks formed.

3.2.3.2 Poly acrylic ester polymer latex

The basic chemical structure of PAE latex polymer is shown in Figure 3.4. PAE is derived from acrylic acid, which reacts with alcohols like ethanol and methanol undergoing esterification, resulting in the formation of poly acrylic ester. Except for the higher air entrainment in PAE systems, the mechanism of action of PAE polymer latex is similar to that in SBR polymer latex.

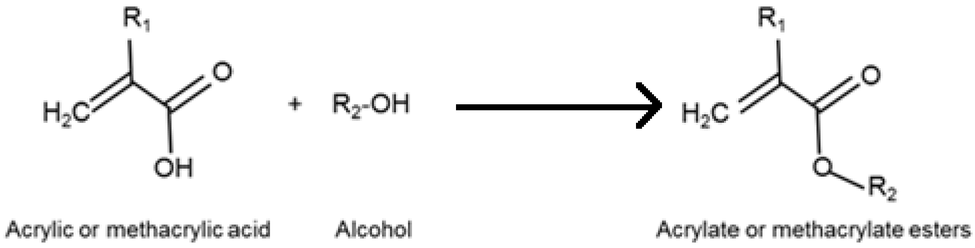


Figure 3.4: Chemical structure of PAE polymer latex (Ohama 1995)

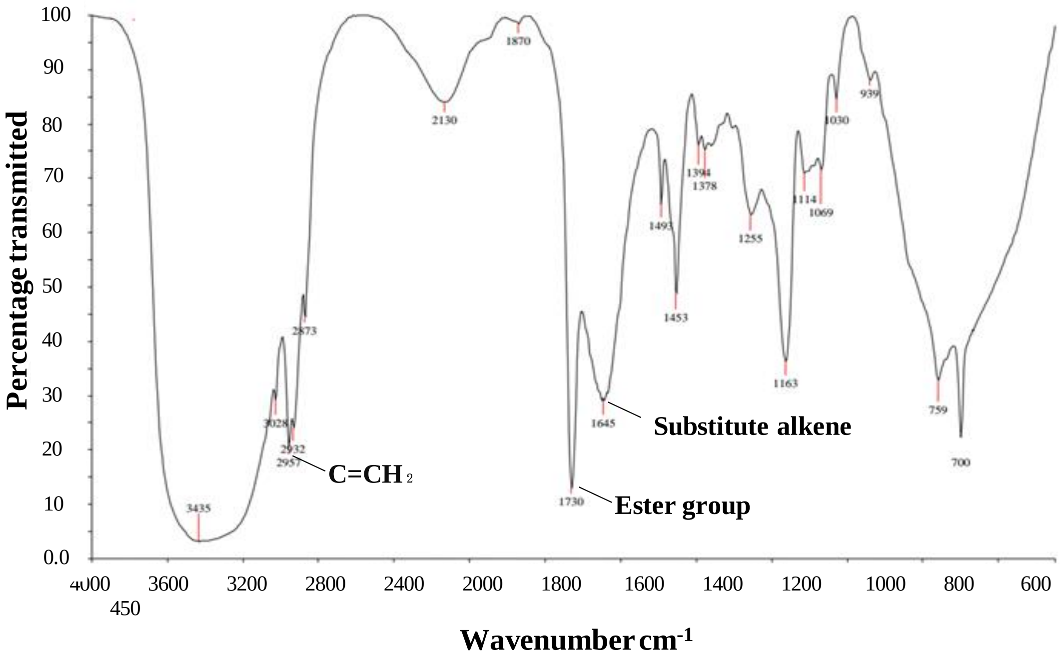


Figure 3.5: FTIR analysis of PAE polymer latex

The PAE polymer latex used in the study had a solid content of 58 %. PAE dosages of 4.5 % and 10 % for the same reasons as SBR, were adopted in this study. FTIR plot of the PAE polymer latex obtained using Spectrum one FTIR Spectrometer – Perkin Elmer is shown in Figure 3.5. The peak at 1730 cm^{-1} show the presence of ester group. The peak at 2957 cm^{-1} reflect the presence of C=CH2, and the peak at 1645 cm^{-1} represents the presence of substitute alkene (Kuptsov and Zhizhin, 1998).

3.2.3.3 Silane modified emulsion polymer (SIL)

Organosilanes or silanes are chemicals that contain at least one carbon silicon (C-Si) bond with a hydrolysable (generally alkoxy) and a non-hydrolysable group (generally alkyl) separated by a spacer. The Si-H bond in silanes are highly reactive with atmospheric water or water adsorbed, forming reactive Si-OH (silanol) species. These silanols react with other silanols formed, developing a stable Si-O-Si bond, which is capable of forming M-O-Si (metal silicon bonds) that narrow the porous channels making it difficult for water to breach further (Moradllo et al. 2016). The hydrophobicity of the substrate to which silane is adsorbed is due to the non-hydrolysable water repellent group present in silane. Silanes are used in various applications such as coupling agents, adhesives, dispersing and cross-linking agents as the hydrolysis and condensation reactions by which the silanes interact and modify the cementitious system occur over the pH conditions prevailing in a cementitious system (Materne et al. 2012). When applied as an integral admixture, silane droplets break or coalesce in an alkaline environment. They react with the silanol rich phases (C_3S and CSH) forming covalent bonds and partially treat the surface. Studies by Kong et al. (2014) show that the reaction of silane on surfaces of non-hydrated cement particle causes deferral hydration (indicated by delay in evolution of heat) but with unmodified porosity. Silane waterproofing agents are expected to offer better UV resistance than the conventional waterproofing agents, as the Si – O bond present in silanes is much stronger than C-O bond present in most other polymers.

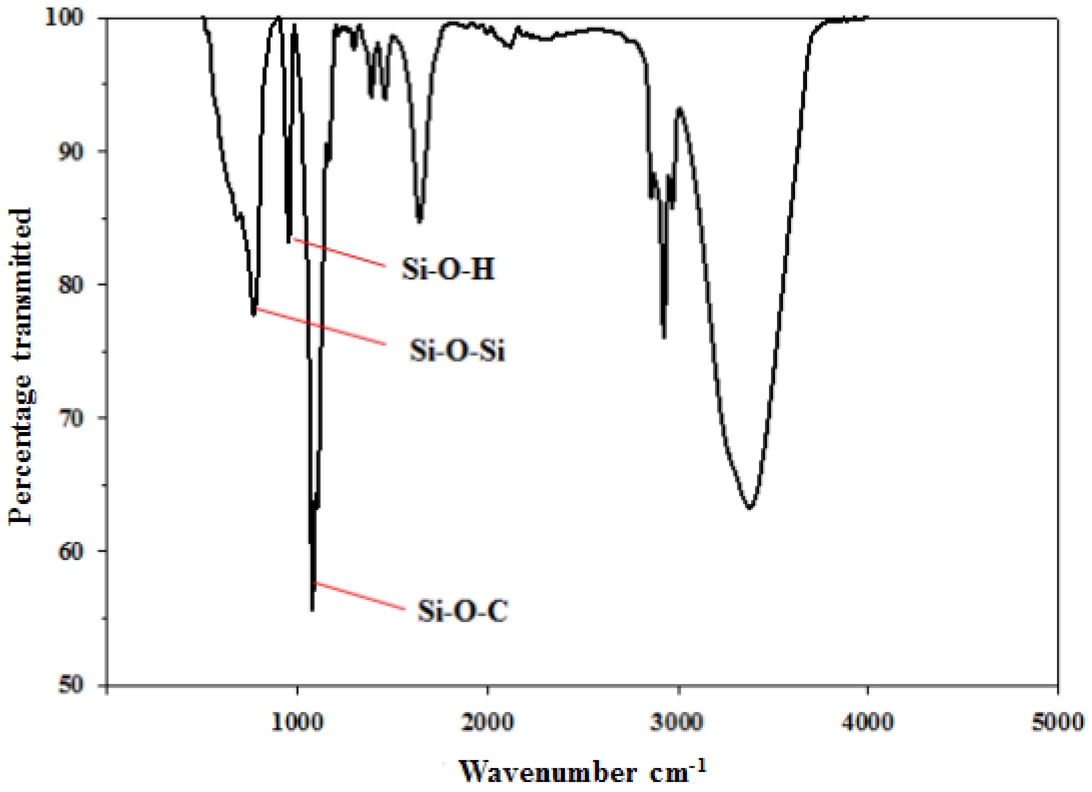


Figure 3.6: FTIR plot of silane polymer representing the bonds formed by silica

The silane modified emulsion polymer used in this study has been processed with silane, an organic backbone of mostly alkyd groups and water to form the emulsion with a solid content of 52.5 %. The FTIR data of silane modified emulsion polymer done using Bruker FT-IR Raman spectrometer is presented in Figure 3.6. The peak intensity at 1000-1100 cm^{-1} represents the Si-O-C bond; and the silanol bond (Si-O-H) is represented by the peaks at 1100, 963 and 768 cm^{-1}; and that at 750 and 500 cm^{-1} represents the Si- O-Si bond (Kuptsov and Zhizhin, 1998).

In this study, the dosage was generally limited to an e/c of 0.25 % for silanes polymer as silane works with an equal workability efficiency (to that of SBR and PAE mortars at 4.5 % p/c) at a lower dosage and the cost is significant.

3.3 Mixture proportion

The casting of all the PMMs was with a constant w/c of 0.45 and a c/s of 1:3. Water content in the latex were accounted for in the mixing water maintaining a constant w/c of 0.45. As discussed earlier, for the SBR and PAE mortars, polymer solid to cement dosages of 4.5 and 10 % (bwoc), and for silanes, a 0.25 % emulsion to cement dosage (bwoc) were adopted. The quantity of various polymers added with water for unit weight of cement (1 kg) is tabulated in Table 4.4.

Table 4.4: Mix proportion of the polymer modified mortar mixes (for 1 kg of cement)

Polymer type	Dosage (% by wt. of cement)	Polymer (kg)	Water (kg)
Control (UCM)	0	0	0.45
SBR latex	4.5	0.10	0.40
	10	0.23	0.3
PAE latex	4.5	0.08	0.42
	10	0.17	0.38
SIL emulsion	0.25	0.0025	0.45

3.4 Mixing procedure

OPC of 53 grade passing through 600 micron sieve was used in the study. The water absorption (determined as per IS:2386 Part 3 – 1963) of the sand and water content (determined from the loss in weight of 250 grams of fine aggregate after being placed in a microwave oven for 3 minutes until no further mass loss occurred) was considered in the calculations to maintain a constant w/c ratio in all mixes.

The mixing of mortar was done in a Hobart mixer of 10 litre capacity. A uniform dry mix of cement and sand was first attained to which the mixture of water and polymeric systems were added. For SBR and PAE mortars, the mixture of water and polymeric latex was added to the dry mortar and mixed until a uniform blend was achieved. Unlike SBR and PAE latexes which are dispersions in water, the SIL is modified polymer emulsion. Due to this fact, the method of mixing needs more caution as it directly influences the workability of the system. It was noticed that in silane modified emulsion polymeric systems, with the same dosage of silane polymer, mixes of variable workability could be obtained at various speeds of mixing (100 - 300 revolutions per minute). Also, water was added to the silane emulsion and not otherwise, at a low shear mixing, as the molecular structure of silanes may break at high speed of mixing causing air entrapment. For effective mixing with the cementitious system, about 80 % of the total mixing water was initially added in the cementitious system, to which emulsion with 20 % water was later added.

3.5 Curing conditions

Studies on polymer modified systems have showed that the extent of formation of the polymer film in the pores, and the interaction between the polymer and the hydration products depends on the moisture conditions and extent of hydration of the cementitious system, both being contingent on the curing (Bothra and Ghugal 2015). A short period of wet curing followed by dry curing is found to be effective in acquiring benefits of polymer addition in a cementitious system, subjective to the polymer type and dosages. To evaluate the dependence of various polymeric systems to curing durations, PMMs along with the UCM, were subjected to three types of curing, all of them being commonly used in the field. They are:

a) Type 1 curing – 1-day of moist curing followed by air curing for 27 days at 25 °C and 65 % relative humidity.
b) Type 2 curing – 7 days of moist curing followed by air curing for 21 days at 25 °C and 65 % relative humidity.
c) Type 3 curing – 28 days of moist curing.

3.6 Accelerated weathering chamber

Owing to applications of repair and waterproofing with exposure to exterior environment and the deterioration of polymers due to UV exposure; the properties of the polymeric system are evaluated at accelerated conditions of weathering. To simulate the long term exposure in exterior environments, specimens were placed in a chamber where UV radiation and high humid conditions were maintained as shown in Figure 3.7 (Krishnan 2014). After the 28 days of curing, the specimens were placed in the chamber and subjected to a cycle of 8 hours of UV light and 4 hours of 90 % relative humidity for a period of 30 days. UV light was provided using UV lamps (wavelength = 340 nm) with an irradiance level of 1.55 $W/m^2/nm$ to replicate the daylight spectrum, as per ASTM G154-16. The relative humidity of 90 % was maintained in the chamber using condensed air produced with a vaporizer. The properties of the mortars tested at normal conditions were re-evaluated after subjecting to critical exposure conditions in the chamber.

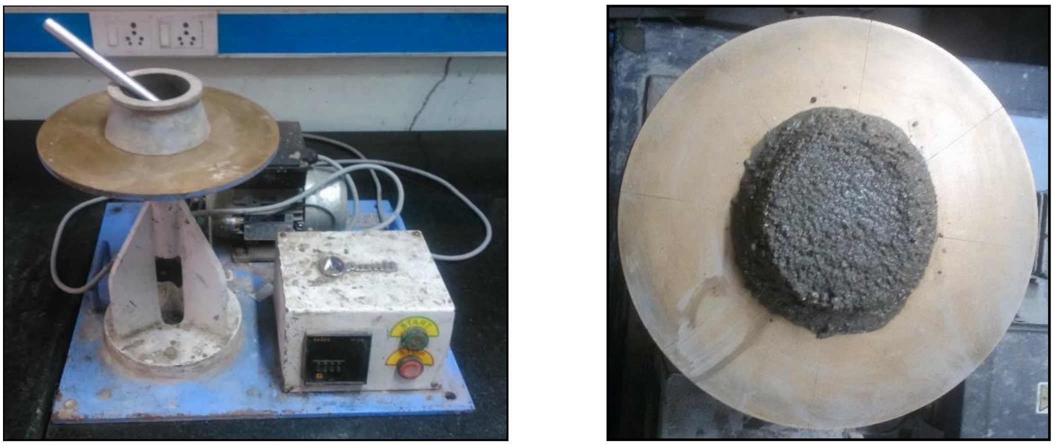
Figure 3.7: Specimens placed in a specially fabricated chamber of 1.5 × 0.5 × 0.5 m for accelerated weathering

3.7 Experimental methods and techniques

As mentioned earlier, the tests were done on the polymer modified mortars for assessing the fresh and hardened properties, durability parameters and microstructural aspects. The fresh properties assessed are the workability (flow test), wet density and setting time. Compressive strength, flexural strength, water permeability, pore structure using MIP (porosity and pore size distribution) and total drying shrinkage were also evaluated for assessing the performance of the PMMs. Microstructural studies were done using SEM and XRD to understand the compositional features and extent of formation of polymer film at various dosages and exposure conditions. The details of the tests done with the specifications, to evaluate the performance of polymer modified mortars are discussed in this section.

3.7.1 Flow test

The workability of the PMMs has been evaluated using the flow table test, as per IS:5512-1983, with a cone of base diameter 100 mm; top diameter of 70 mm and height of 50 mm as shown in Figure 3.8. The increase in the spread diameter, as a percentage of the initial base diameter, after been subjected to 25 jolts was recorded as the flow.



(a) (b)

Figure 3.8: Flow table setup: (a) Testing apparatus (b) Flow of mortars

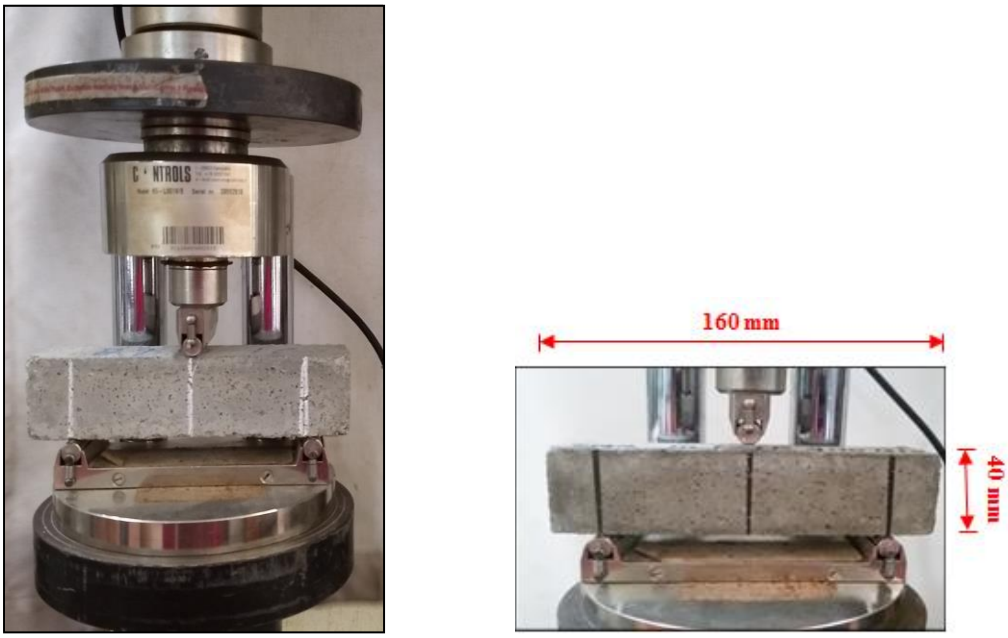
3.7.2 Compressive strength

The compressive strength was tested, as per IS 4031 (Part 6) – 1988 reaffirmed 2005, on 50 mm cubes, in a testing system with 250 kN capacity, as shown in Figure 3.9. The compressive strength of the cubes was tested on the 28th day after casting at normal conditions of testing, and on the 60th day after casting for accelerated weathering conditions testing (after exposure to 28 days of various curing types followed by exposure to weathering conditions until 60th day of casting). The loading rate adopted was 1000 N/sec (as per IS 4031), and the average strength of 3 cubes tested was reported as the compressive strength of the mortar.

Figure 3.9: Compressive strength test setup

3.7.3 Flexural strength

Flexural tests were performed as shown in Figure 3.10; the average strength of 3 specimens being reported as the mean flexural strength. The testing procedure is as per IS: 4031 (Part 8) – 1988 reaffirmed 2005, on prisms of 160 × 40 × 40 mm, at a loading rate of 20 N/sec. Third-point loading was done on the specimens over a span of 120 mm, using a testing system of 15kN capacity.



(a) (b)

Figure 3.10: Flexural strength testing (a) Experimental setup (b) Specimen view

3.7.4 Water permeability

In this study, water permeability of the mortar specimens was tested by allowing water to pass through under pressure. The procedure was as per DIN 1048 (Part 5), where 150 mm cubes were exposed either from above or below, to a distilled water under a pressure of 0.5 N/mm^2 acting normal to the casting face, for a period of three days (as shown in Figure 3.11). Immediately after the pressure is released, the specimen is removed and split down the centre with the face exposed to water facing down; and the maximum depth of penetration in the direction of slab thickness is measured in mm. The test procedure does not yield any absolute value for the coefficient of performance but assesses the connectivity of pores and compares the water permeability of different mortars.

(a) (b)

Figure 3.11: DIN 1048 water permeability test setup (a) Test setup (b) Split surfaces showing water penetration

3.7.5 Total drying shrinkage

Prisms of 160 mm × 40 mm × 40 mm were used to evaluate the drying shrinkage properties of the mortar. The specimens were tested as per ASTM C 596 – 2007, as shown in Figure 3.12. The specimens after been subjected to the curing durations, were kept in a controlled environment of 25 °C and 65 % relative humidity, and the reduction in the length of the specimens was noted every day using a dial gauge of sensitivity 0.001 mm, until the shrinkage values got stabilised.

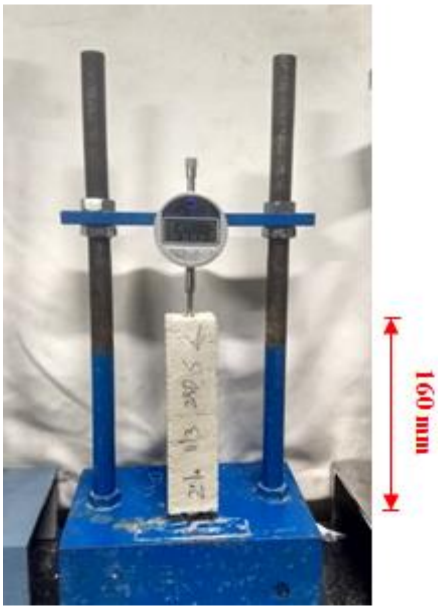


Figure 3.12: Test setup for measuring of shrinkage

3.7.6 Microstructural studies

Microstructural studies were done to evaluate the composition of mortars and micro-level modification at various curing types, dosages and exposure conditions which could validate the performance at various test conditions. The samples for microstructural studies were prepared as per ASTM C1723-10, after 28 days, and were preserved in isopropanol for a period of 4 days after which they were dried and stored in a desiccator for micro-level analysis. Micro-level studies were done using SEM, MIP and XRD each of which is explained in the following section.

3.7.6.1 Scanning Electron Microscopy

The scanning electron microscope produces images of a sample by scanning the surface with a focused beam of electrons. It could also be provided with the EDAX facility, which is a characterization technique based on the principle that every element has a specific atomic structure due to which the X-Ray emission spectrum will have specific peaks that can be used to identify the elemental composition. X-Ray emission spectra from the samples are obtained by letting a beam of electrons or X-Rays fall on the sample which would interact with them stimulating the electrons to higher energy levels. On stabilisation of these electrons wherein they come back to the lower energy levels, the difference of energy would be released as X-Ray, which would be captured by the detector; and specific peaks would be used to identify the elemental composition. The difference in compactness of the microstructure of PMMs at various curing types and exposure conditions were analysed using a SEM facility shown in Figure 3.13.The machine confirmed to a resolution of 3 nm (30 kV, SE image mode) and a magnification range of 10x to 3,00,00x. The EDAX facility of the instrument was also utilised to study the elemental composition of mortars.

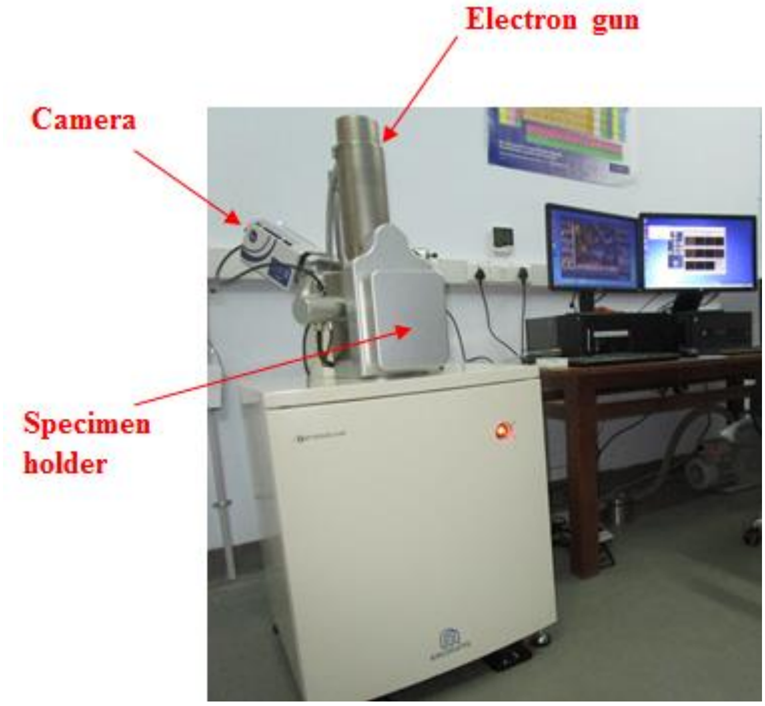


Figure 3.13: SEM instrumental set up (GENESIS-1000/1100 supplied by EMCRAFTS)

3.7.6.2 Mercury Intrusion Porosimetry (MIP)

In MIP, mercury being a non-wetting liquid, is forced to enter the pores of the material using external pressure as it will not enter the pores spontaneously by capillary action. The pressure needed to force mercury into the pores is inversely proportional to the pore size; for example: mercury intrudes easier in macro pores than in micro pores. From the pressure versus intrusion data, the equipment generates volume and size distributions using Washburn equation which states as

$D = -4 \Upsilon \cos \theta / P$……………………………………………………………………………Eq. 3.1

where,

D = minimum diameter of the pores that the mercury would intrude at a pressure P,

Υ = surface tension of mercury, and θ = non-wetting angle.

By knowing the volume of mercury that fills the pores at each pressure, the volume of the pores in the corresponding sizes can be known. Volume of mercury entering the pores is determined using a mercury penetrometer, which is an electrical capacitance dilatometer sensitive to a volume change of mercury less than 0.1 µlitre. The dilatometer consists of a stem of glass that is an insulator; filled with mercury, a conductor; and is plated with a metal which is also a conductor. The two conductors: mercury and the metal plating are separated by the glass, forming a coaxial capacitance. As the mercury intrudes the sample due to the external pressure, the capacitance changes. The decrease in capacitance is proportional to the volume of mercury entering the sample, which in turn is proportional to the volume of the pores.

The MIP instrument used for the study consists of two parts as shown in Figure 3.14. Mercury intrusion into the samples up to pressure of 140 kPa is carried out in the first cycle followed by intrusion at pressures up to 400 kPa in the second part. The cumulative volume of the mercury intruded and the pore size data obtained from the instrument are used to plot the distribution of various pore sizes in the sample, from which the porosity of the material can be inferred.

Figure 3.14: MIP setup (Pascal Mercury Porosimeter from ThermoFisher Scientific)

3.7.6.3 X-Ray Diffraction (XRD)

XRD is an analytical technique used for characterization by phase identification of a crystalline material. It basically uses the constructive interference of an X-Ray and crystalline sample, where X-rays generated in the cathode ray tube, when directed to the sample, produce constructive interference when Bragg's law condition is satisfied. As the sample and detector in the instrument are rotated, the intensity of the reflected X-ray is recorded. The detector converts this signal to a count rate against the angle of rotation of the detector.

In the present study, techniques of XRD are used to study the degradation of PMMs at elevated temperature conditions to understand the critical temperature conditions above which the deterioration of the system occurs. The XRD facility of Metallurgical and Materials Engineering (MME) Department was used for the study. Samples were measured in the range of 5 °C $\leq 2\Theta \leq$ 65 °C at 40 mA and 30 mV.

3.7.7 Elevated temperature testing

The application of PMMs in environments, where high temperature conditions can arise, must be considered for testing, especially to assess the properties beyond the glass transition temperature of the polymer. The deterioration of the polymer system beyond this temperature can disrupt the concrete system as a whole. The polymers used in the study have glass transition temperatures falling below 200 °C for which the properties of PMMs were studied at elevated temperatures starting from 100 °C to 600 °C. The elevated temperature conditions were achieved in a muffle furnace, which could generate environments of up to 1000 °C. The specimens were placed in the furnace where the temperatures were set to elevate to the desired high temperature (at a heating rate of approximately 5 °C/minute) and then maintained for an hour. The temperature was then reduced and the samples cooled to room temperature (at a cooling rate of approximately 3 °C/minute) were tested to check on their properties. The study at elevated temperatures was confined to the mechanical properties of the mortar where the retention in compressive and flexural strengths at each of the higher temperature was determined and the critical temperature beyond which the properties failed drastically was identified for each of the polymeric systems. At fire 2conditions, the combustibility and flammability of the PMMs were analysed by visual inspection.

3.8 Summary

This chapter outlines the details and specifications of the materials used and the mixing procedures adopted for the casting of specimens. It also discusses the various exposure conditions to which the specimens were exposed to and the test setup for each of those conditions. Techniques used to characterize microstructural, mechanical and durability properties, are also detailed.

CHAPTER 4

INFLUENCE OF CURING ON THE PERFORMANCE OF PMMS AT STANDARD CONDITIONS

4.1 Introduction

Studies on polymer modified cementitious systems have shown that the extent of the formation of the polymer film on the pores, and its interaction with the hydration products depends on the moisture conditions and extent of hydration of the cementitious system. It is noted that both these factors (i.e. moisture conditions and extent of hydration) are contingent on the curing (Bothra and Ghugal 2015). Though polymeric systems are widely used in various civil engineering applications, the recommended curing rarely accounts for the differences in the polymer type. This could be the reason for many polymeric systems not performing to the expected level in the field. Thus, there is a need to study the combined effect of dosage and curing conditions for polymeric systems for ensuring adequate functionality in the applications.

This chapter includes a detailed discussion of the results from various tests on PMMs. Fresh properties such as workability, initial and final setting times, and wet densities; mechanical properties such as compressive strength and flexural strength; and total drying shrinkage and water permeability of the PMMs were evaluated and analysed. The micro-level modifications under various curing regimes were assessed using SEM and MIP.

4.2 Fresh properties of PMMs

The influence of polymer additions on the fresh properties of cementitious mortars, such as workability and wet density of mortars, and setting time of cement pastes, are discussed in this section.

4.2.1 Workability

Workability of the cementitious system was assessed using the flow test and the results are reported in Table 4.1. The addition of polymers results in an increase in workability of the cementitious system. It is seen that the workability of all the PMMs was higher than that of the UCMs with same w/c ratio of 0.45, and improved with an increase in the dosage of the polymers, as seen in the studies by Krishnan (2014) and Devarsh (2015) on PMMs. As discussed, the combined influence of polymers, air entrainment and dispersing effect of the surfactants present in the latexes enables more flow in the polymeric systems (Ohama 1995). Among the PMMs, the silane offered better enhancement of workability than other polymeric systems even though the dosage was lower. This has been attributed to the high adsorption and steric repulsion of silane polymer (Kong et al. 2015). The silanol formed by the hydrolysis of silane provides good bonding on the cement grains, and the alkyl group on silanes provide high steric repulsion. Also, the hydrophobic nature imparted to the cement grains by the adsorption of silanes may give rise to water repellence causing more water to be available for flow and workability (Materne and Buyl 2004).

Table 4.1: Flow of UCM and PMMs evaluated using flow table test

Type of polymer	Dosage (% bwoc)	Increase in flow (%)
UCM	0	30
SBR	4.5 p/c	110
	10 p/c	130
PAE	4.5 p/c	110
	10 p/c	130
SIL	0.25 e/c	140

4.2.2 Wet density

The wet density and air content of various PMMs have been measured and reported in Table 2.2. It is seen that the wet density reduced with the introduction of polymers into the cementitious system. The gravimetric air entrainment data, shown in Table 2.2, indicates that the lower densities in PAE are due to higher air entrainment in these systems.

Table 4.2: Wet densities and air contents of PMMs

Mix ID	Dosage of polymers (% bwoc)	Fresh unit weight (kg/m^3)	Gravimetric air entrainment (%)
UCM	0	2589	1.0
SBR	4.5 p/c	2239	2.4
	10 p/c	2120	3.0
PAE	4.5 p/c	1634	8.3
	10 p/c	1645	6.1
SIL	0.25 e/c	2249	1.1

4.2.3 Initial and final setting times

The incorporation of polymers generally extends the setting time of mortar due to the delay in hydration by polymer film formation around the cement particles (Knapen and Gemert 2009). The film encapsulates the cement grains and hinders the migration of water resulting in delayed hydration. This effect was observed in all polymeric systems, with longer setting times for higher dosages of the polymer, as reported in Table 4.3. However, the setting time of cement paste modified with the silane was lower than that of UCM, which seems to contradict the observations of Kong et al. (2015) where a retarding effect was seen with silane polymers in the early hydration though they also reported that the setting times were comparable to that of UCM after 120 hours of hydration.

Table 4.3: Initial and final setting times of PMMs at various dosages

Mix ID	Initial setting time (hour : minutes)	Final setting time (hour: minutes)
UCM	5:00	8:20
SBR 4.5 %	4:00	12:00
SBR 10 %	8:30	12:30
PAE 4.5 %	5:50	13:30
PAE 10 %	13:20	15:00
SIL 0.25 %	4:40	5:40

4.3 Microstructural studies using SEM and MIP

SBR and PAE mortars at 10 % p/c dosage were prepared as mentioned in Chapter 3 and studied along with the mortars having silanes at 0.25 % e/c and unmodified mortar.

4.3.1 Surface imaging using SEM

To study the difference of morphology by the addition of polymer, SEM analysis was done on UCM and PMMs subjected to the same curing conditions, as shown in Figure 4.1. It was noted that the microstructure in the unmodified mortars was coarser and uniform. Figure 4.1(b) corresponding to the SBR modified system shows an interconnected network of polymer-hydration products with open spaces in a dense structure. The results were found to conform to the findings of Knapen et al. (2004) that reported that polymer modified systems had distinct hydrated phases compared to the reference mortar. This difference in morphology highlights the nature of hydrates formed in the PMMs. Nevertheless, from Figure 4.2, it is clear that the silane modified mortar has minor differences in the microstructure compared to UCMs, with layers of discontinuous polymer film.

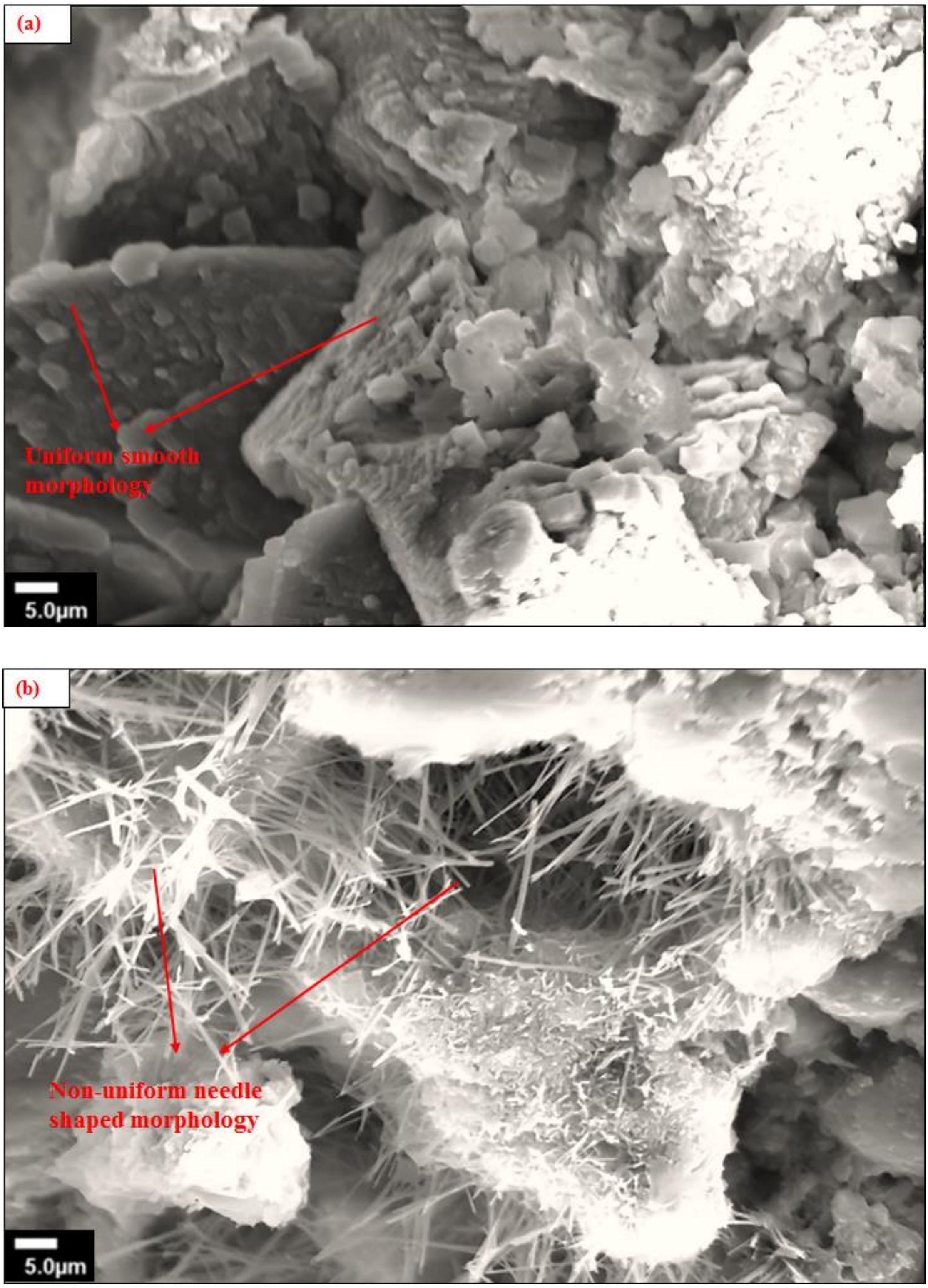


Figure 4.1: SEM images of (a) UCM and (b) SBR polymeric system (with 10 % p/c) after 28-day wet curing

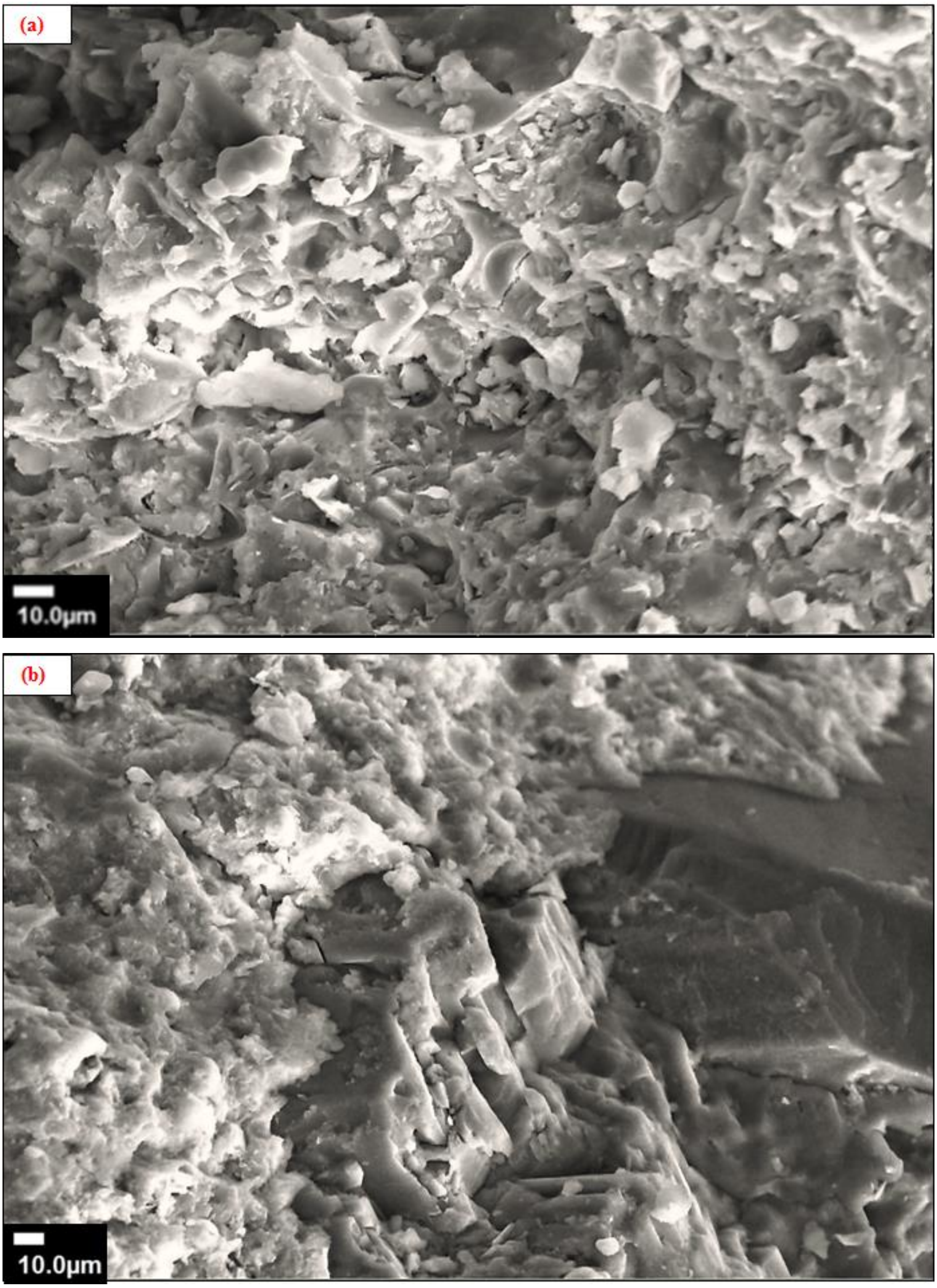


Figure 4.2: SEM images of silane mortars (0.25 % e/c) showing similar morphology for samples subjected to (a) 1-day and (b) 7-day wet curing

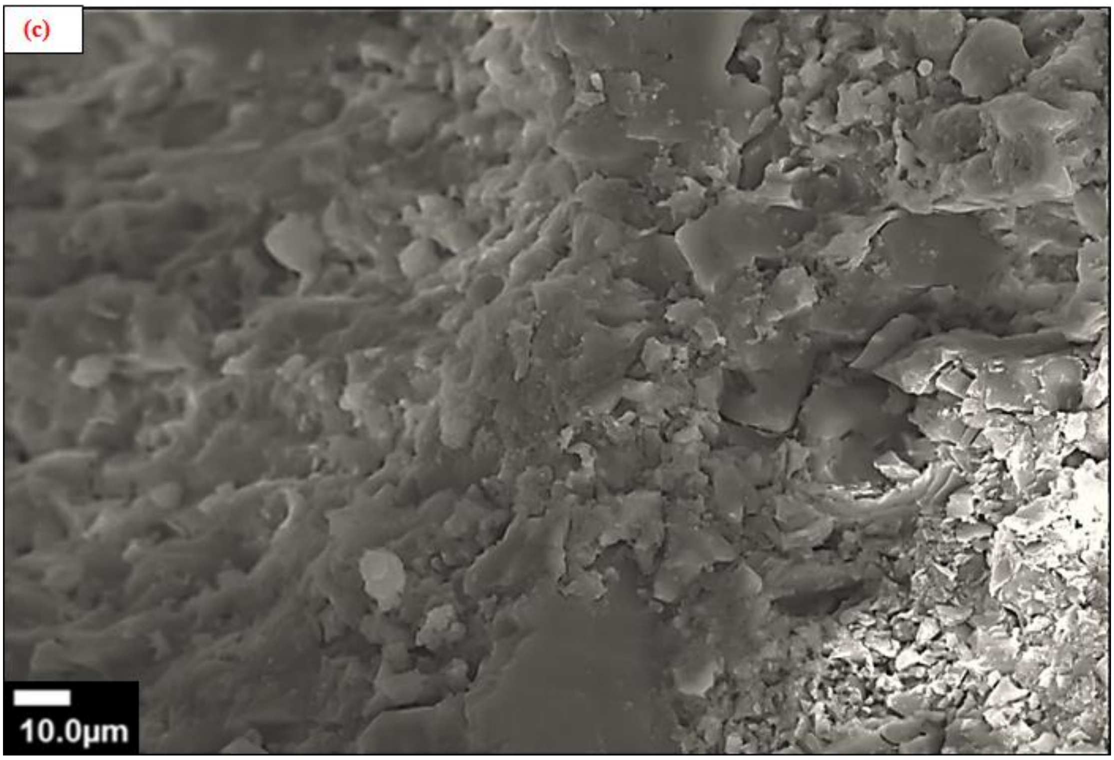


Figure 4.2: SEM images of silane mortars (0.25 % e/c) showing similar morphology for samples subjected to (c) 28- day wet curing

It was also noted that the microstructure evolution in polymeric systems of SBR and PAE showed a dependence on the period of curing. Samples subjected to extended periods of wet curing (i.e., 28 days) showed more pronounced presence of hydrates (with calcium to silica ratio greater than 1, in most areas of the surface when evaluated through EDAX), which could lead to the localization of polymer film formation, and reduce the expected performance impact of the polymer on PMMs. With shorter periods of wet curing (i.e., 1 day) followed by air curing up to the age of 28 days, there is a more uniform microstructure conducive for the continuous polymer film (Figure 4.3). This suggests that the compactness of the microstructure of the PMMs may progressively decrease with an increase in the duration of wet curing. Silane mortars (as seen from Figure 4.2) retained similar microstructure with an increased period of wet curing. This can be attributed to the interaction of silane polymers with the binder phase occurring through a process of hydrolysis followed by condensation. Both the processes are dependent on the alkyl group (that impart hydrophobicity to the cement surface or sand) on the silane molecule and on the pH of the system (Brinker 1988), which are less influenced by the period of wet curing.

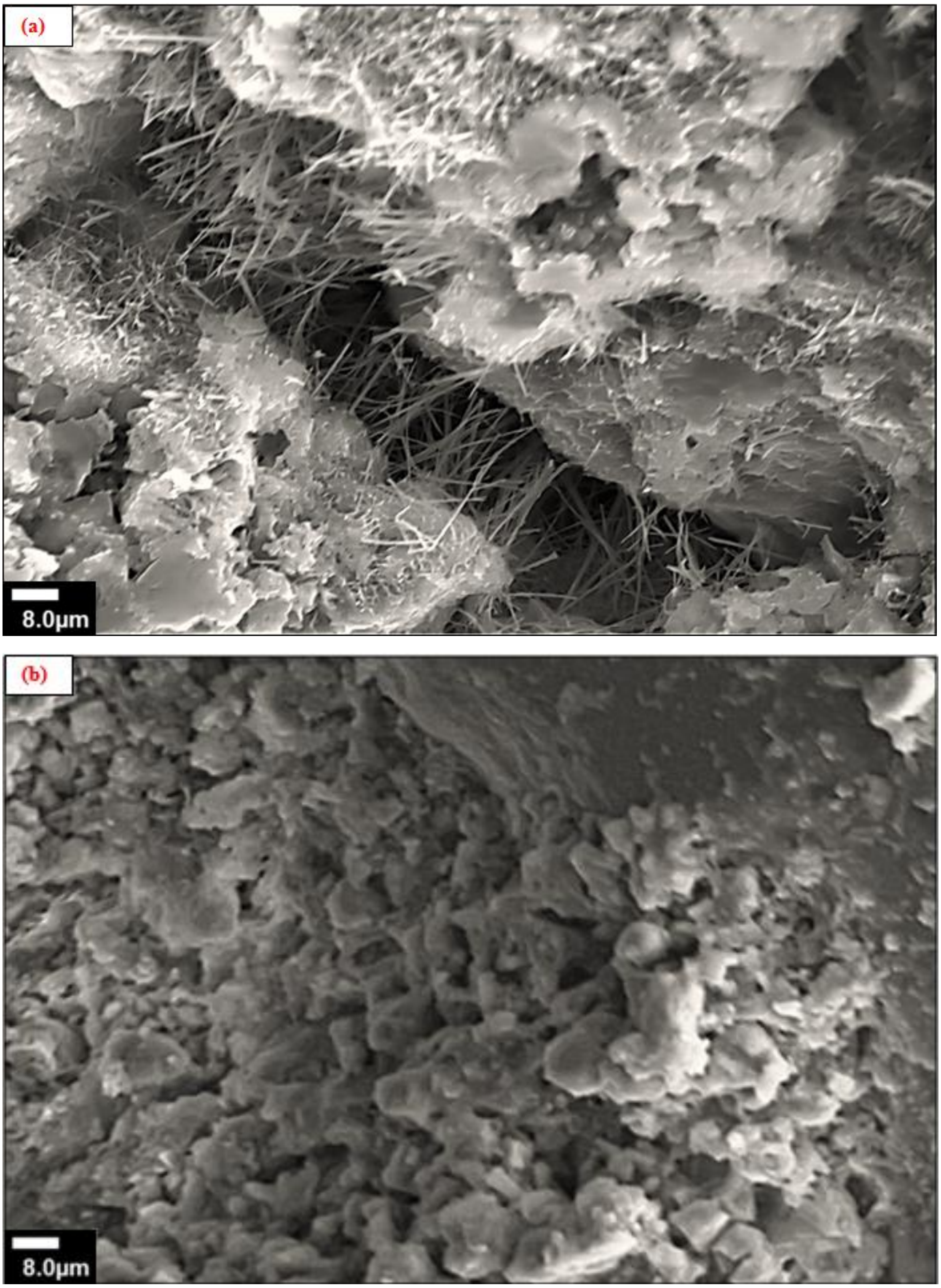


Figure 4.3: SEM images of SBR mortars subjected to (a) 28 days and, (b) 1 day of moist curing

4.3.2 Porosity studies using MIP

Porosity and pore size distribution of cementitious systems play an important role in mass transport and hence the durability (Bungey and Millard 1996). The porosity and compactness of the mortars at various test conditions were studied using MIP where the pore size, density, distribution of pores and other porosity related characteristics were analysed. In unmodified mortars, porosity generally decreases with progressive development of pore structure during the hydration process (Ishida et al. 2007). The results of the porosity studies carried out using MIP on PMMs show that curing has a major impact on the porosity and pore size distribution of the cementitious system, as expected. From the pore size distribution of SBR mortar samples subjected to various curing types (Figure 4.4), it is seen that there is a refinement in pore structure with an increase in the period of wet curing. The differential intruded volume plotted as the ordinate in the graph is a measure of the volume of pores in the specific pore sizes provided in the abscissa. Samples subjected to Type 1 curing (i.e., 1 day of wet curing followed by air drying), had higher pore volume in the size range of 0.05 to 0.5 µm, and specimens cured till 7 and 28 days of wet curing, possessed higher pore volume in the smaller size ranges of 0.005 to 0.05 µm. It is also acknowledged that pore sizes in the ranges of 0.002 to 0.01µm affect the capillary pressure, which control the shrinkage performance, compared to the pores in the size ranges of 0.01 to 10 µm, which control the permeability of the system (Tanabe et al. 2008). Thus, limited wet curing (i.e., 1 day) leading to higher volume of larger sizes of pores can result in higher permeability.

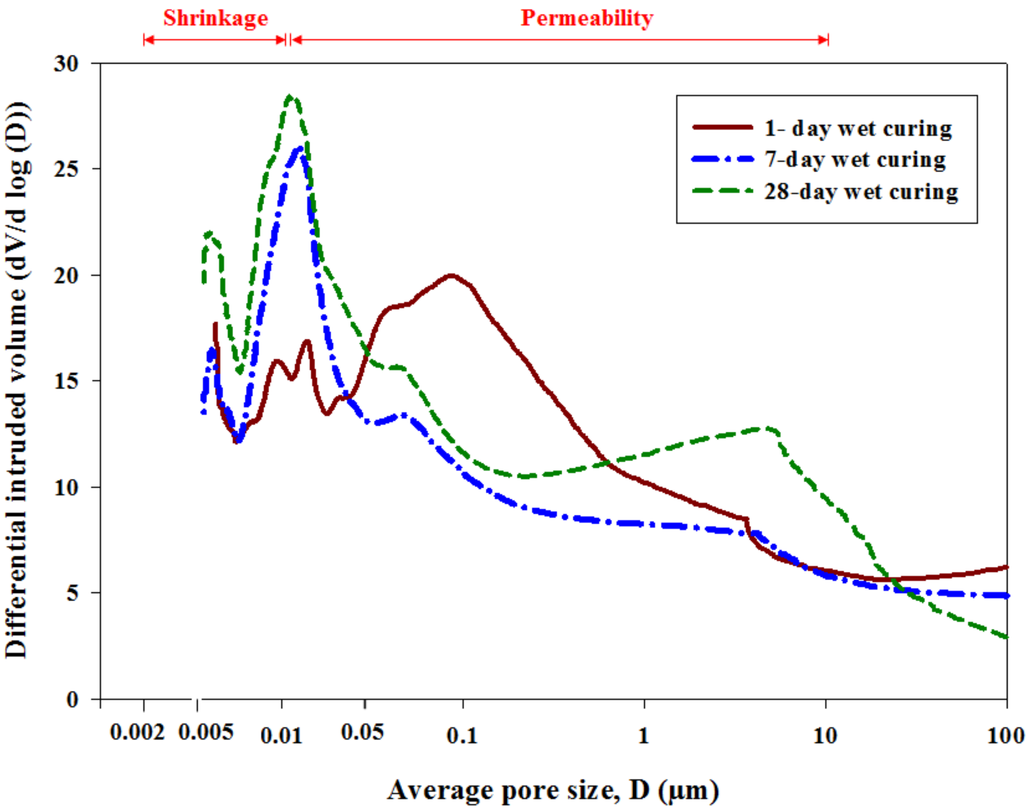


Figure 4.4: Pore size distribution of SBR mortar samples (10 % p/c) subjected to 1 day, 7 days and 28 days of wet curing

For comparing the volumes of different sizes of pores in UCM and various PMMs, the plots of the cumulative volume of mercury intruded into various samples of PMMs and UCM are presented in Figure 4.5. It was seen that the cumulative volume of micro (< 1 µm) and macro-pores (> 1 µm) in all PMMs was higher than the UCM except for SBR mortars in the micro pores. The porosity level in the conventional polymeric systems of SBR and PAE was 3 times that of the UCM. Silane modified systems showed a pore structure similar to that of UCM with negligible porosity in the ITZ and larger pores (10-100 µm), and higher porosity in capillary and gel pore ranges (< 10 µm). SBR and PAE mortars had a different pore size distribution with the former showing coarser pores in the range of 10 µm to 100 µm, and PAE having capillary pores of 1 to 10 µm.

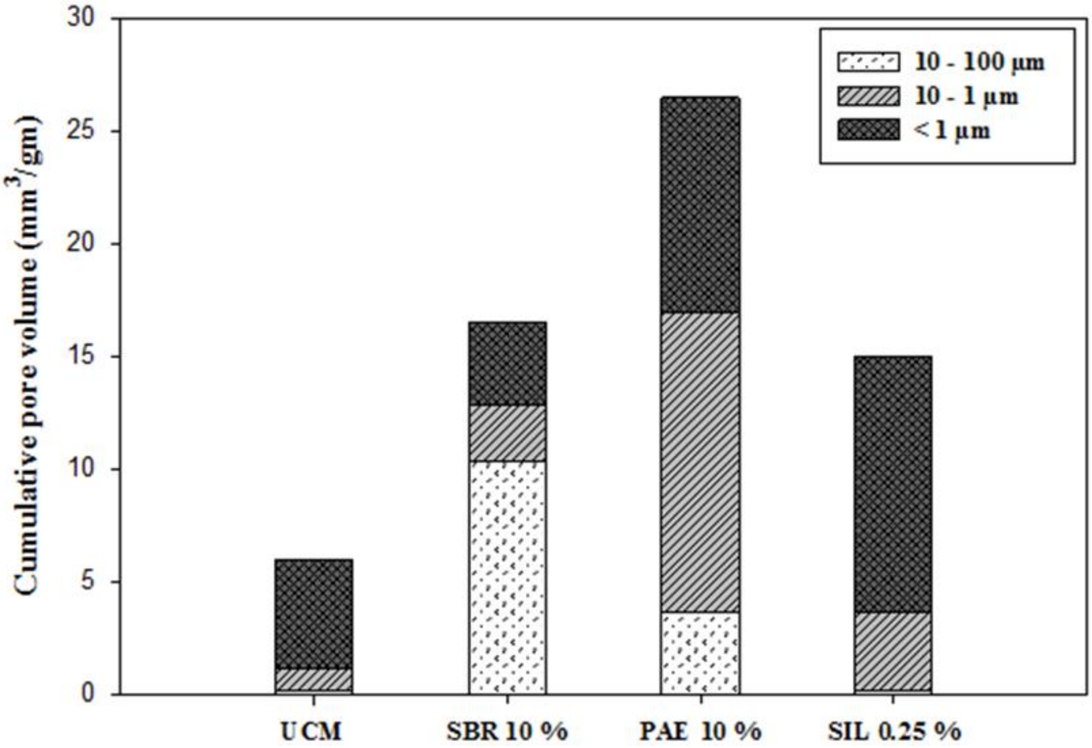


Figure 4.5: Porosity evaluation of UCM and PMMs using MIP data at 28 days of wet curing

4.4 Engineering properties

Polymeric systems being commonly used for repair, waterproofing and plastering, a moderate mechanical strength is necessary. To evaluate the effect of the polymer additions on mechanical properties, the compressive and flexural strength of mortars have been evaluated. The cube specimens were tested at 28 days after casting, after being subjected to various types of curing conditions as discussed in Section 3.5.

4.4.1 Compressive strength

Incorporation of polymers leads to a reduction in compressive strength, with the decrease being largely dependent on the dosage of the polymer used and curing conditions. The compressive strengths of UCM and the PMM tested at various dosages and curing types are given in Table 4.4. The mean compressive strength of 3 specimens tested at 28 days are reported in each case (Figure 4.6), along with the standard deviation.

Table 4.4: 28-day mean compression strengths of UCM and PMMs for various curing conditions, and standard deviations

Type of mortar	Mean compressive strength (MPa) and standard deviation at 28 days		
	1 day wet curing + 27 days air curing	7 days wet curing + 21 days air curing	28 days wet curing
UCM	26.3 (±0.7)	51.4 (±2.7)	53.8 (±2.1)
SBR 4.5 % p/c	29.7 (±0.7)	34.2 (±1.4)	30.3 (±0.9)
SBR 10 % p/c	26.3 (±0.1)	25.6 (±1.3)	23.4 (±2.5)
PAE 4.5 % p/c	28.6 (±0.4)	38.2 (±0.1)	39.3 (±0.4)
PAE 10 % p/c	22.6 (±0.5)	27.2 (±0.2)	23.5 (±0.8)
SIL 0.25 % e/c	27.5 (±0.5)	33.9 (±1.4)	37.8 (±0.9)

All PMMs showed lower compressive strengths than the UCM, at all dosages and curing conditions, which further reduced when higher dosages of polymer were used. This is in accordance with the results reported in literature, where the decrease in compressive strength of PMMs is attributed to the reduction in the gel space ratio by the introduction of polymers (Ma and Li 2013). This explains the reason for the higher compressive strength in SBR and PAE mortars with limited wet curing periods (1 day and 7 days). The results are consistent with the results of Krishnan (2014) and Kumar (2015), where limited periods of wet curing were found to give higher compressive strength. A prolonged period of wet curing (as in Type 3) reduces the polymer film formation and pore refinement, resulting in lower compressive strength with less benefits of polymer addition. However, the silane modified mortars showed higher compressive strength with an extended period of wet curing (28 days) as with the case of UCM. The 28-day compressive strength of silane mortars increased as the wet curing period increased from 7 days to 28 days. At lower dosages of polymer, SBR and PAE mortars with shorter periods of wet curing (1 to 7 days), followed by air curing, exhibited higher 28-day compressive strengths than the UCM subjected to similar conditions.

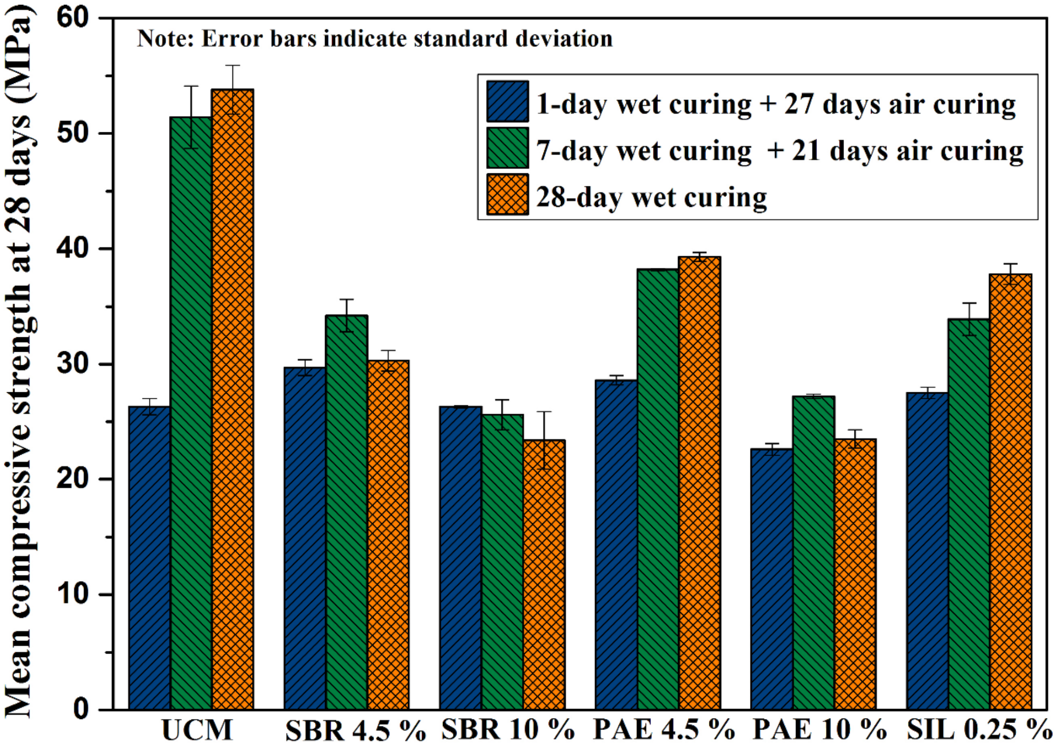


Figure 4.6: Mean compressive strengths of PMMs for various curing types

4.4.2 Flexural strength

The flexural strength of UCM and PMMs tested at 28 days are reported in Table 4.5 and Figure 4.7.

Table 4.5: Flexural strength of UCM and PMMs for various curing conditions

Type of mortar	Mean flexural strength (MPa) (and standard deviation)		
	1 day of wet curing + 27 days of air curing	7 days of wet curing + 21 days of air curing	28 days of wet curing
UCM	5.7 (±0.2)	6.4 (±0.7)	7.2 (±0.9)
SBR 4.5 % p/c	4.7 (±0.7)	5.0 (±0.4)	5.2 (±1.0)
SBR 10 % p/c	5.3 (±0.6)	4.9 (±0.4)	4.7 (±0.3)
PAE 4.5 % p/c	6.3 (±0.9)	7.3 (±0.3)	6.2 (±0.1)
PAE 10 % p/c	5.3 (±0.3)	4.9 (±0.0)	4.7 (±0.4)
SIL 0.25 % e/c	6.4 (±0.6)	6.9 (±0.2)	6.8 (±0.2)

For SBR and PAE modified systems, lower dosages of polymer (say, 4.5%) with 7 days of wet curing (Type 2) gave higher flexural strength. Also, the flexural strength of PAE mortars was higher than the SBR mortars at normal conditions. This can be attributed to the higher carboxylic ion content in PAE that reacts with calcium ions forming an interwoven network that could impart higher flexibility to acrylic modified systems (Tian et al. 2013). At higher dosages of polymer (say, 10 %), the flexural strength was higher for 1-day wet curing possibly due to better binding between the cementitious matrix and the polymer film. The flexural strength of PAE mortars reduced with an increase in dosage for all curing types, contrary to SBR, which showed an enhancement of flexural strength at higher dosages with 1-day wet curing. As seen from Table 4.2, the gravimetric air content of PMMs with PAE was nearly 100 % higher than PMMs with SBR at similar dosage levels (10 %), which could be the reason for the drop in flexural strength. As discussed, limited periods of wet curing (1 and 7 day) induce formation of better polymer film resulting in a higher flexural strength for all polymeric systems. Silane mortars showed higher flexural strength with 7-day wet curing; however, the variation with respect to the curing types was minimal. It can be inferred that the silane polymeric systems were less influenced by the curing type, compared to SBR and PAE systems, which were found to be highly sensitive. Higher dosages (10 %) of polymer and longer wet curing periods (28 days) result in poor flexural strengths for SBR and PAE mortars. Hence, it is understood that when the polymer content is higher, the mortar could have higher flexural strength when the wet curing is limited to 1 to 7 days.

It was also noted that PAE at 4.5 % p/c and silane at 0.25 % e/c dosages gave better flexural strength behaviour than UCM despite lower compressive strength. Similar trends were reported in the study by Krishnan (2014), and the higher flexure strength was attributed to the bridging action of polymers within the continuous cementitious matrix.

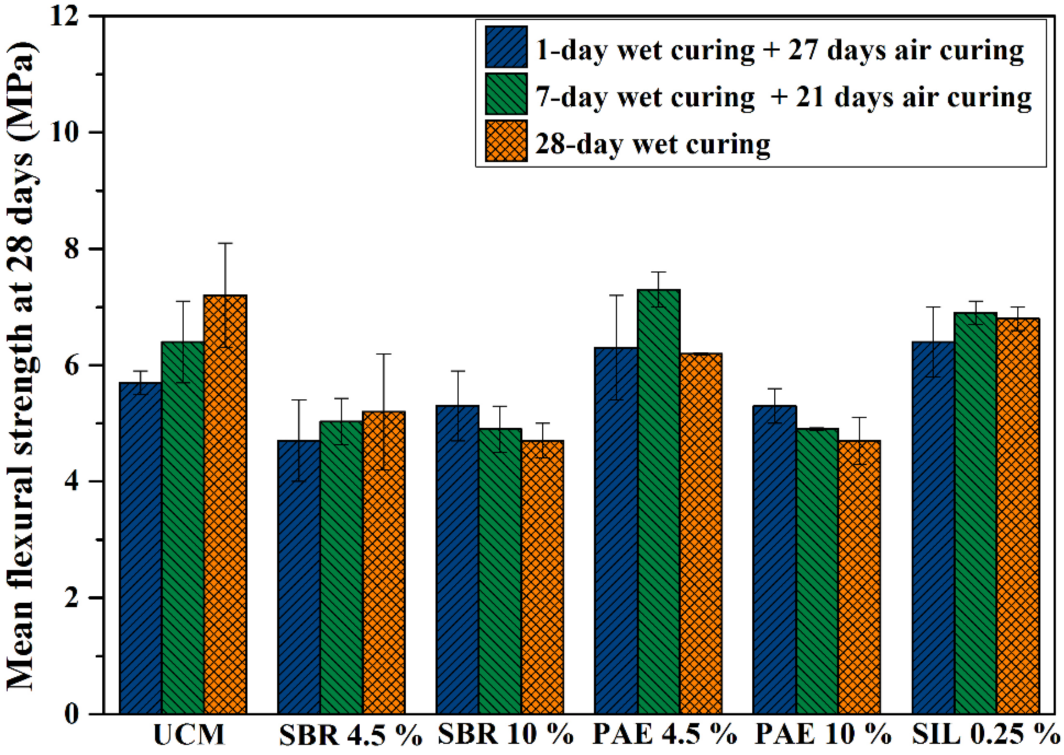


Figure 4.7: Mean flexural strengths of PMMs exposed to various curing types

4.5 Total drying shrinkage

Lower shrinkage is a desirable characteristic in any cementitious systems, especially in the case of repair mortars, to maintain adequate compatibility with the concrete substrate. With prolonged wet curing periods, there would be an increase in hydration extent and lower pore sizes; both can result in an increase in shrinkage strain.

Shrinkage strains of the mortars evaluated after 1, 7 and 28 days of wet curing are presented in Table 4.6, and represented in Figures 4.8 to 4.12 and in log-scale axis in Figures 4.13 to 4.17, where the markers represent the shrinkage values of 3 mortar samples and the solid line represents the mean shrinkage strain, for each polymeric system. For SBR and PAE, the shrinkage was higher with longer durations of wet curing due to the possibility of higher amount of water in the capillary pores. Longer periods of wet curing (28 days) result in higher shrinkage in PAE systems than in SBR systems. The higher porosity of PAE mortars along with smaller pore sizes (as identified from MIP) could lead to an increase in mass loss and increased capillary pressure causing the higher shrinkage. This effect was, however, not seen with silane mortars, which had lower shrinkage with longer periods of wet curing, as seen in Figure 4.12. The hydrophobic nature of the alkyl groups in conjunction with the alkoxy reactive sites in silanes causes water repellence, as well as adherence to the cementitious system, so that moisture loss occurs without any increase in shrinkage, even with prolonged durations of wet curing. It is also noted that the sensitivity of the shrinkage of polymeric systems based on the period of wet curing followed the order of PAE > SBR > SIL systems (Table 4.6). The PAE modified systems exhibited higher shrinkage with an increase in polymer dosage, at all types of curing (Figure 4.10 and Figure 4.11).

Table 4.6: Total drying shrinkage strain of UCM and PMMs at various dosages and curing conditions

Type of mortar	Total drying shrinkage (micro strain) with various durations of wet curing after 60 days of drying		
	1 day wet curing + 27 days air curing	7 days wet curing + 21 days air curing	28 days wet curing
UCM	450	440	537
SBR 4.5 % p/c	360	320	636
SBR 10 % p/c	310	230	737
PAE 4.5 % p/c	480	780	827
PAE 10 % p/c	583	985	1250
SIL 0.25 % e/c	477	774	583

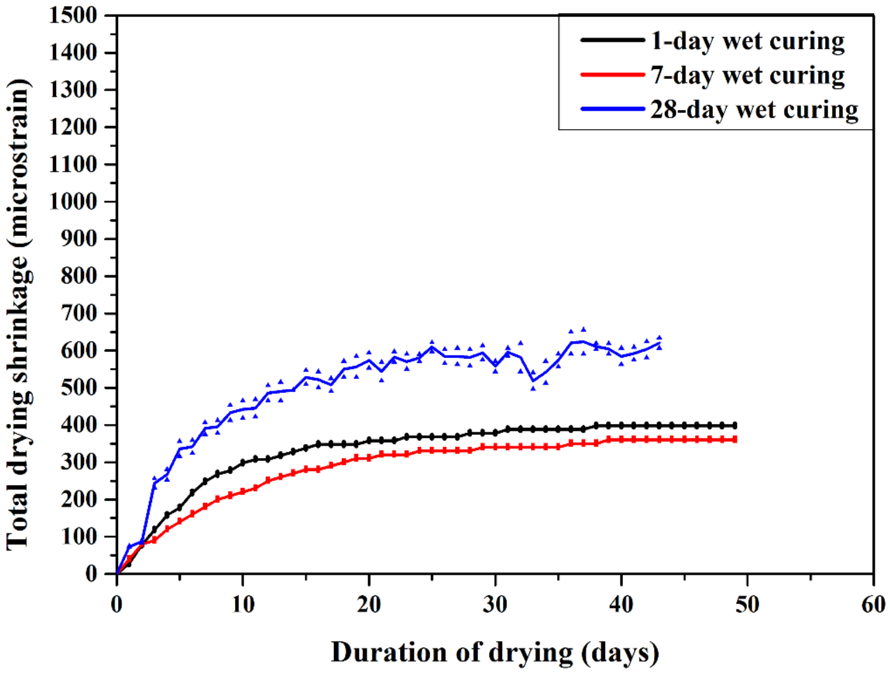


Figure 4.8: Shrinkage strain evolution for SBR 4.5 % p/c for various curing types

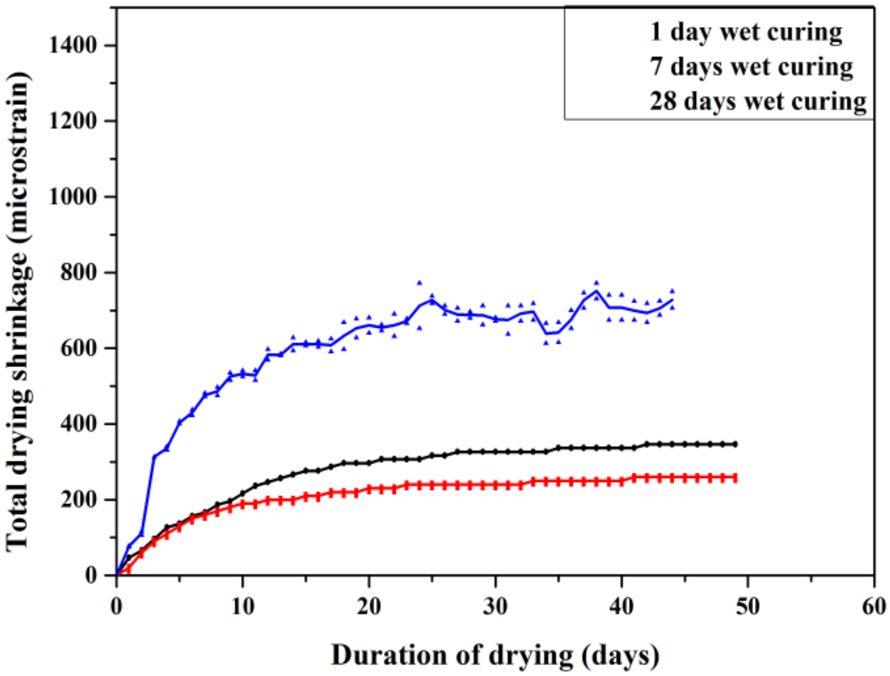


Figure 4.9: Shrinkage strain evolution for SBR 10 % p/c for various curing types

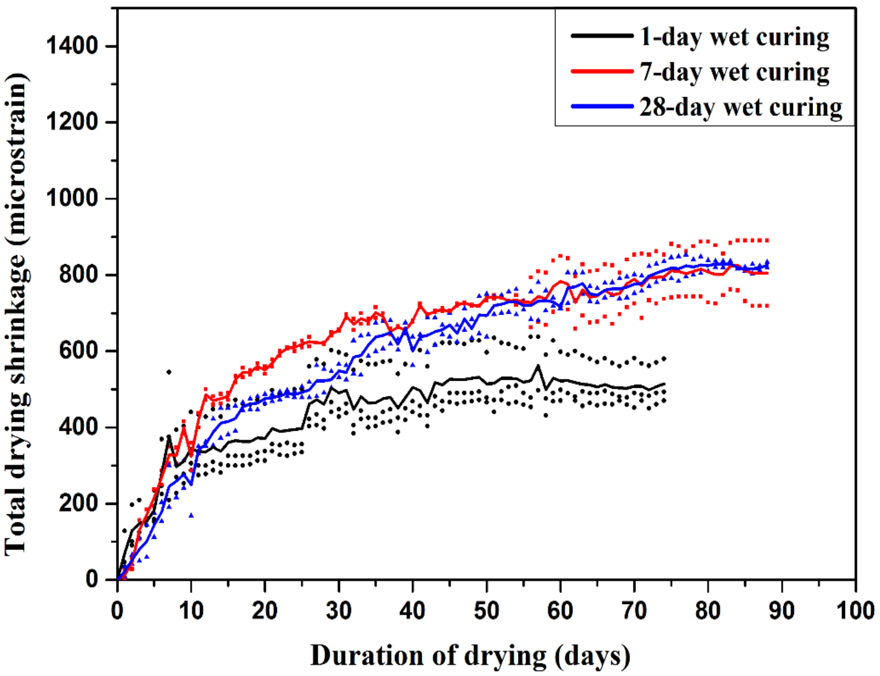


Figure 4.10: Shrinkage strain evolution for PAE 4.5 % p/c for various curing types

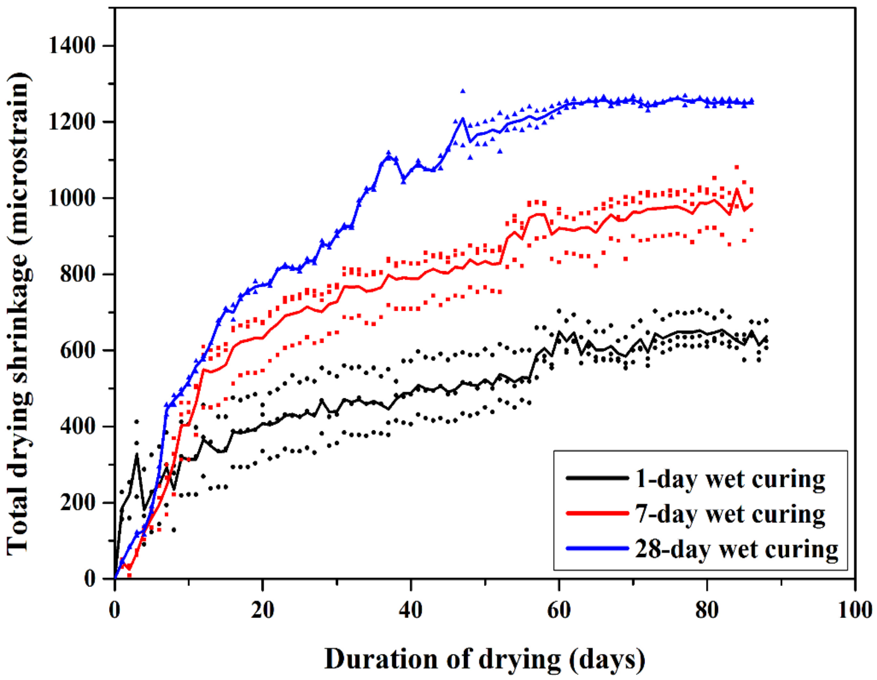


Figure 4.11: Shrinkage strain evolution for PAE 10 % p/c for various curing types

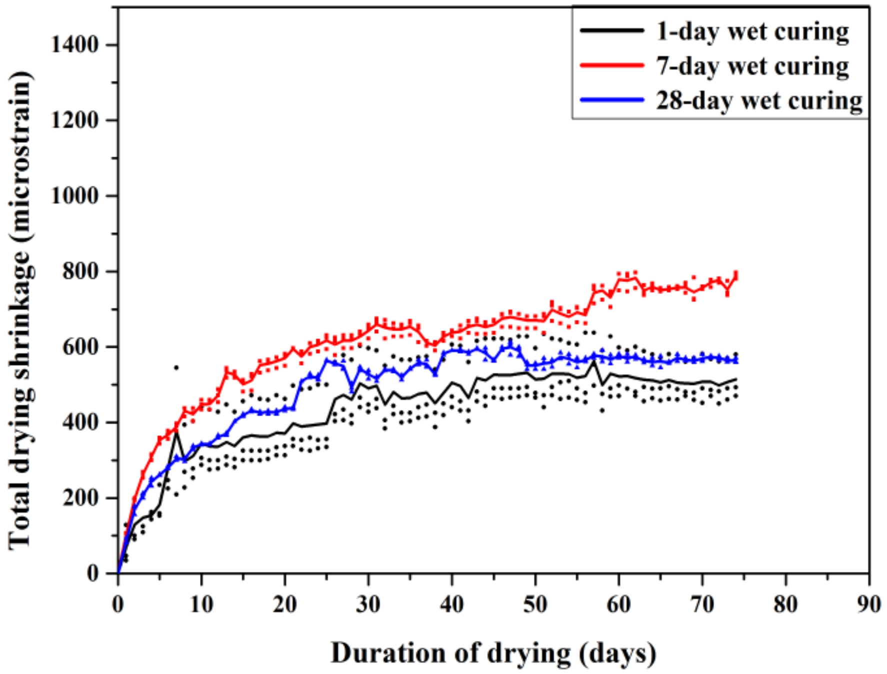


Figure 4.12: Shrinkage strain evolution for SIL 0.250 % e/c for various curing types

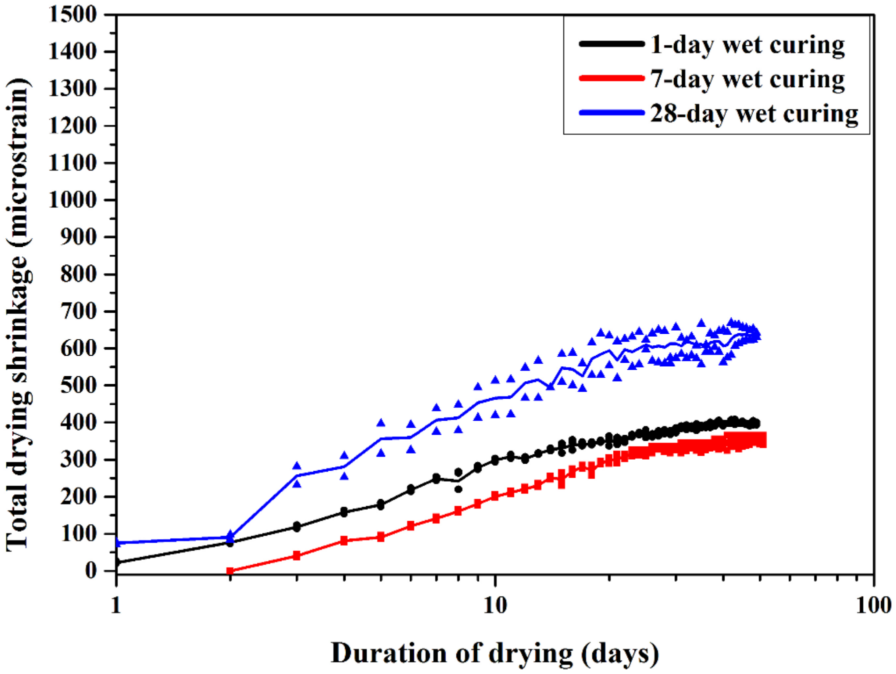


Figure 4.13: Shrinkage strain evolution for SBR 4.5 % for various curing types, represented on log-scale

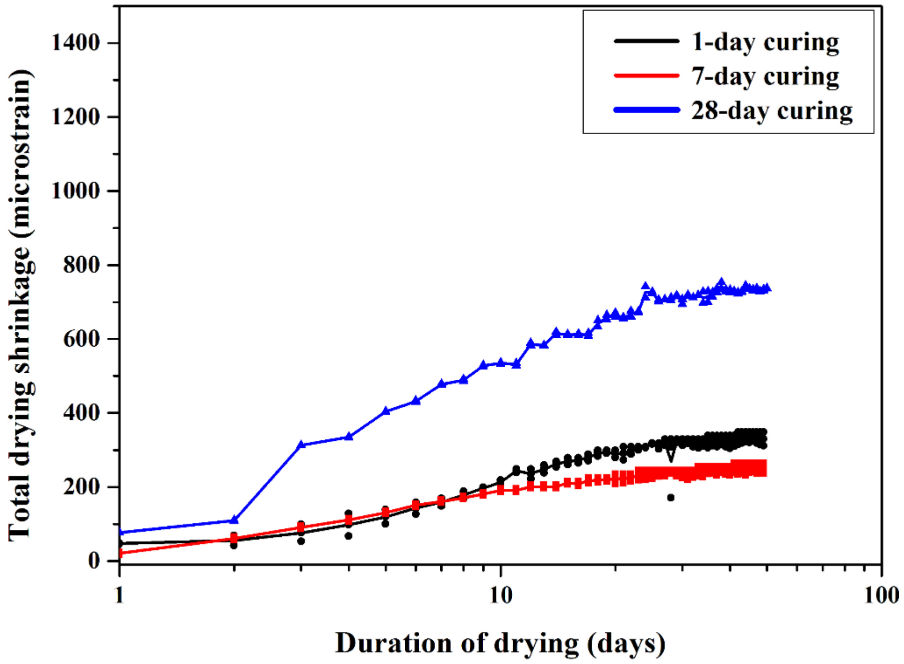


Figure 4.14: Shrinkage strain evolution for SBR 10 % for various curing types, represented on log-scale

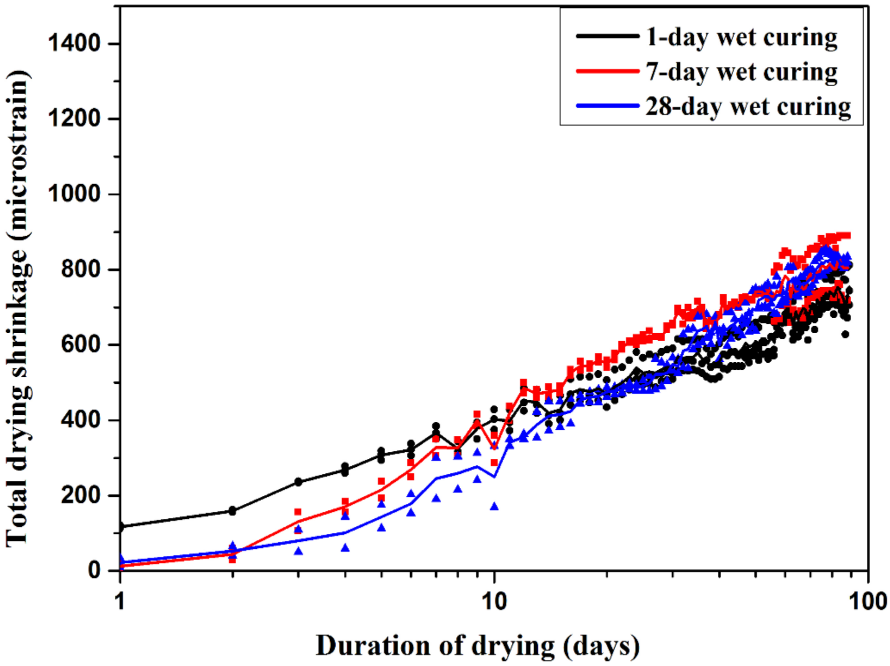


Figure 4.15: Shrinkage strain evolution for PAE 4.5 % p/c for various curing types, represented on log-scale

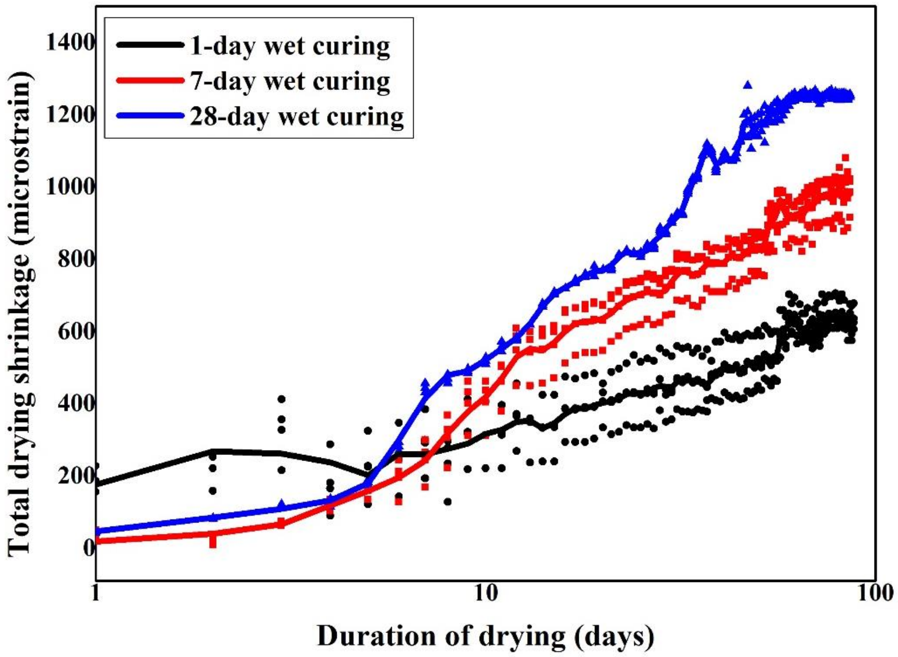


Figure 4.16: Shrinkage strain evolution for PAE 10 % p/c for various curing types, represented on log-scale

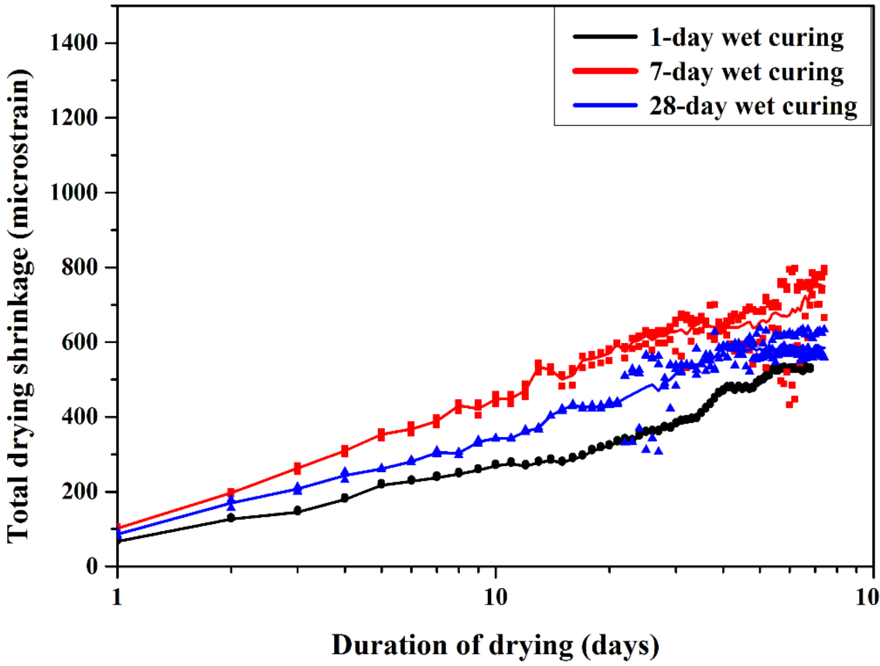


Figure 4.17: Shrinkage strain evolution for SIL 0.25 % e/c for various curing types, represented on log-scale

Among the PMMs, SBR mortars showed lower shrinkage with less than 7 days of wet curing periods, hence, they appear more suitable for applications where long duration of curing is not feasible. For systems with prolonged wet curing conditions being obligatory, silane polymeric systems, which showed lower shrinkage strain at such conditions, can be recommended.

4.6 Water permeability results

From the water permeability results of PMMs (Table 4.7) shown in Figure 4.18, it is seen that SBR mortars showed lower depth of penetration of water than UCM while silanes gave a comparable penetration with UCM. PAE mortars had a higher depth of penetration at all curing types and dosages. The leaching of polymer (indicated by higher Total Organic Carbon (TOC) values of PAE polymer, as reported in Krishnan 2014) and high gravimetric air content associated with higher dosages of acrylic based polymer can be the controlling factor affecting the water permeability characteristics. The depth of penetration of water in SBR mortars reduces when longer wet curing periods (28 days) were provided; whereas, PAE mortars was lower with shorter wet curing periods (1 days and 7 days). This difference in performance of SBR and PAE mortars can be on the account of the leaching of PAE polymers noted at longer durations of wet curing (28 days), whereas SBR mortars do not address the problem of leaching. The high water permeability of PAE mortars at longer periods of wet curing (28 days) can be on the account of the leaching of polymers at such curing conditions. The water permeability results of silane mortars were similar for all curing durations showing less effects of curing in these systems.

Table 4.7: 28-day water permeability results of UCM and PMMs subjected to various curing conditions

Type of mortar	28-day depth of penetration of water (mm)		
	1 day wet curing + 27 days air curing	7 days wet curing + 21 days air curing	28 days wet curing
UCM	119	81	78
SBR 4.5 % p/c	58	18	16
SBR 10 % p/c	38	17	16
PAE 4.5 % p/c	140	143	150
PAE 10 % p/c	128	138	121
SIL 0.25 % e/c	118	139	118

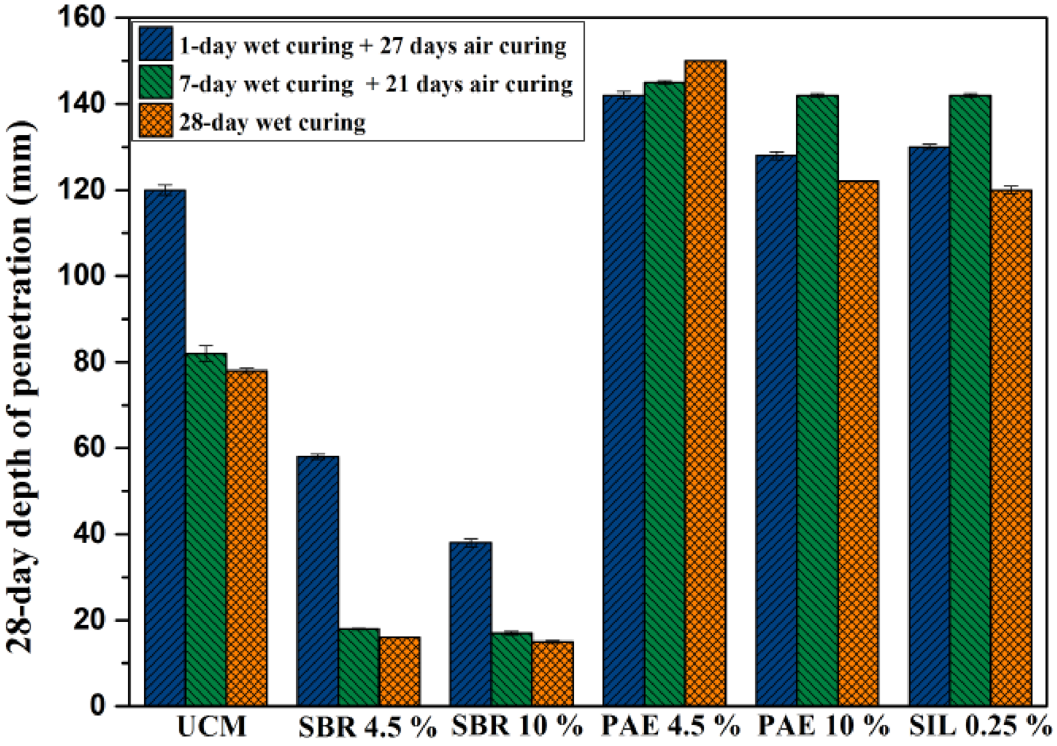


Figure 4.18: 28-day water permeability test results of UCM and PMMs tested at various curing types and dosages

SBR mortars showed reduced penetration of water at all curing durations; signifying excellent permeability resistance and adaptability for water proofing applications.

4.7 Effect of dosage on the performance of SIL mortars

Generally, SIL polymers are used in the e/c range of 0.15 % - 0.5 % as recommended by the manufacturer, owing to the higher cost. It was already seen that the workability and strength properties of SIL PMMs compare well with those of the conventional polymeric systems when tested at lower dosages. However, in this part of the study, the effect of dosage on the performance of SIL PMMs is specifically assessed, covering the the mechanical properties, shrinkage and water permeability.

Compressive and flexural strengths of silane modified systems tested at e/c dosages of 0.25 %, 0.6 %, 1 %, 2 % and 3% are presented in Figures 4.19 and 4.20, respectively. As seen from Figure 4.19 and Figure 4.20, a substantial enhancement in compressive strength was seen with an increase in dosage up to 0.6 % and flexural strength up to dosages of 1 %. However, with further increase in dosage, the increase in compressive strength was lower, identifying 2 % as the saturation dosage level. It was also noted that there is a shift in the preference of curing from longer periods of wet curing at lower dosages to shorter periods of wet curing at higher dosages for higher mechanical properties.

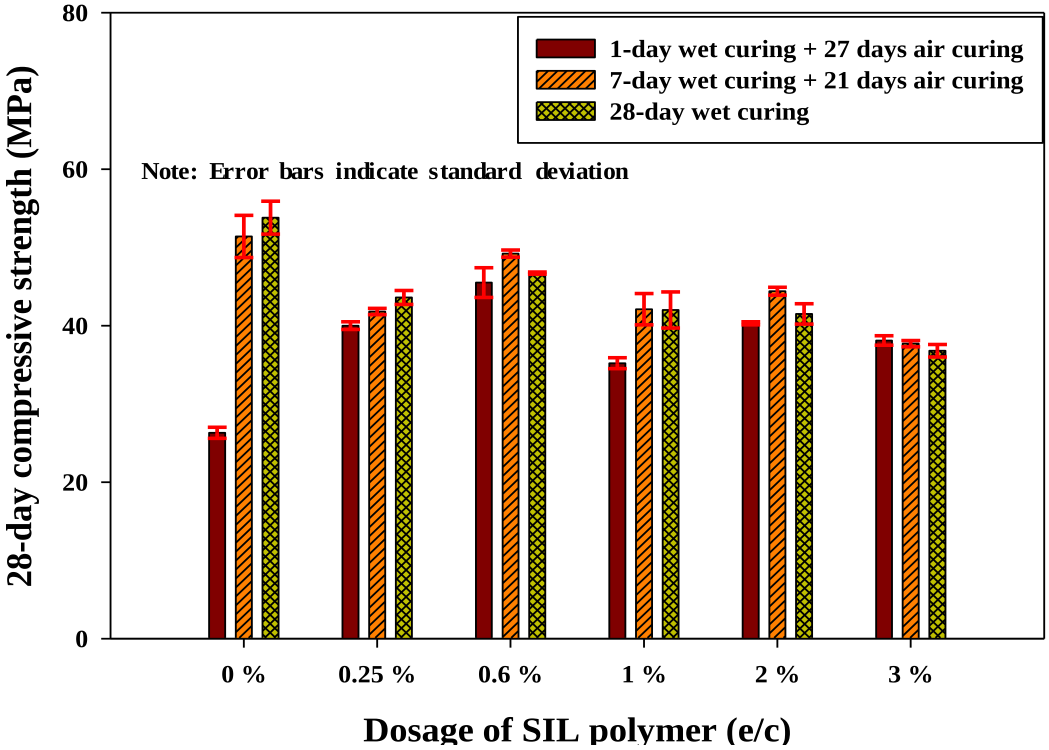


Figure 4.19: Compressive strengths of SIL PMMs at various curing types for dosages of 0.25 % to 3 % e/c

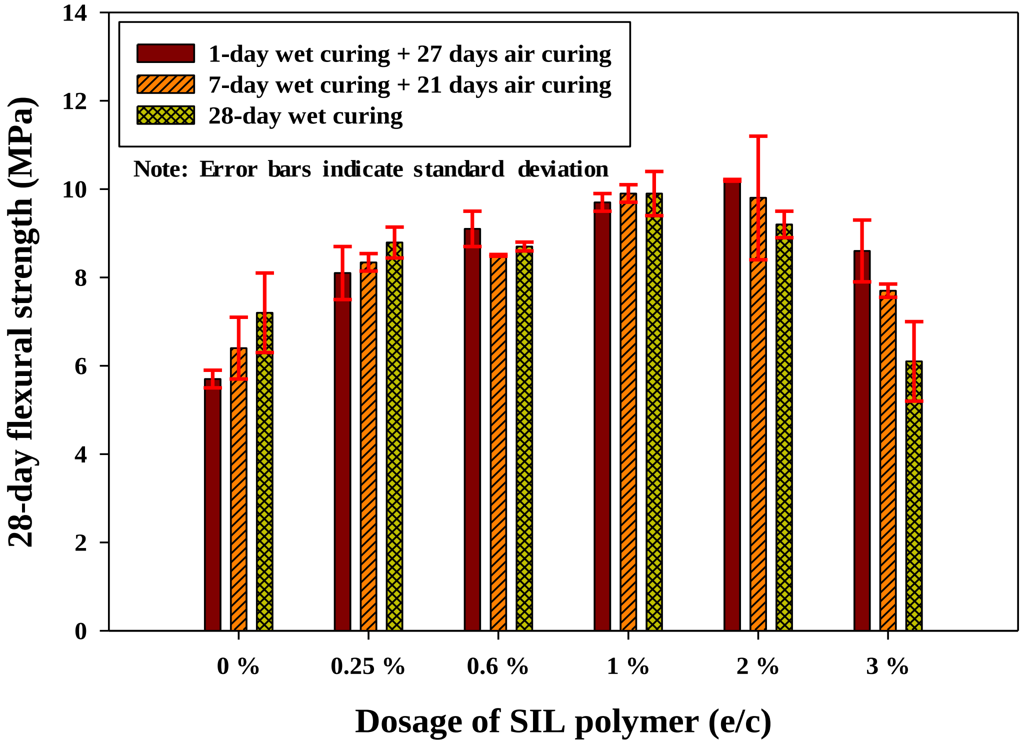


Figure 4.20: Flexural strengths of SIL PMMs at various curing types for dosages of 0.25 % to 3 % e/c

From the shrinkage and water permeability results plotted in Figure 4.21 and Figure 4.22, respectively, it is observed that higher dosages of SIL polymers resulted in lower permeability with less impact on drying shrinkage. However, lower permeability and shrinkage are seen for 1-day wet cured specimens, for all dosages of SIL mortars.

Thus, it can be inferred that the dosages of silane employed in mortars influence the shrinkage significantly while the effect is lower on water permeability and mechanical properties. Considering the high cost involved, the usage of high dosages (1 % e/c) of silanes may not be feasible in most applications of polymeric systems, for which lower dosages such as 0.25 % e/c with shorter periods of wet curing (< 7 days) can be recommended as it outperforms the properties of conventional polymeric systems at even such lower dosages.

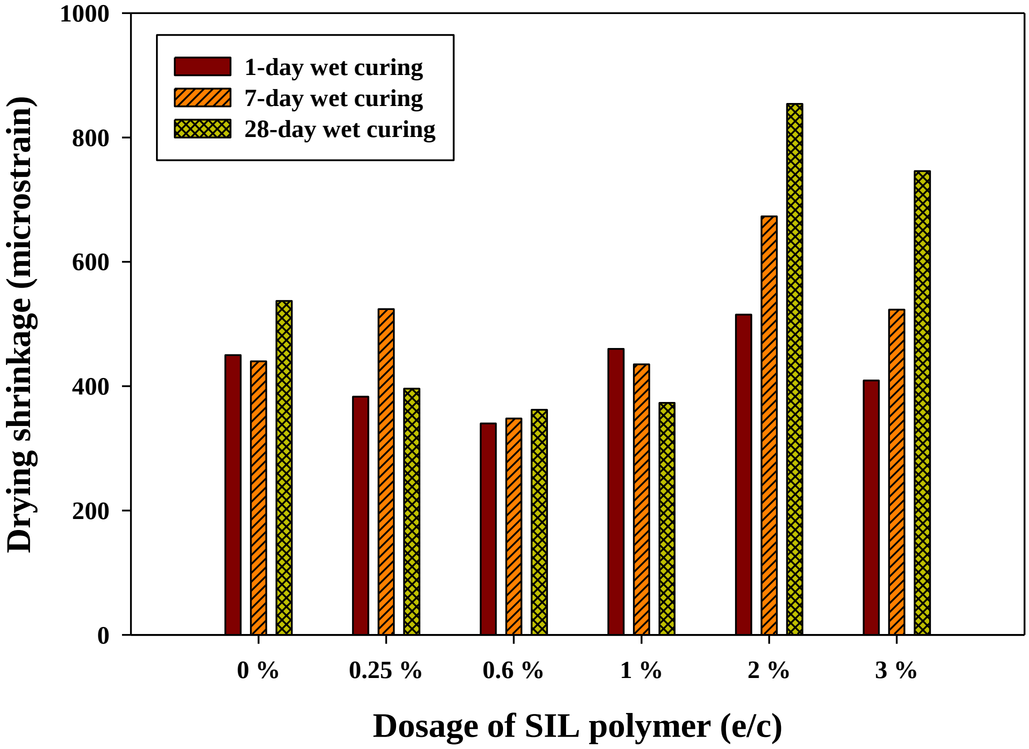


Figure 4.21: Shrinkage of SIL PMMs at various curing types for dosages of 0.25 % to 3 % e/c

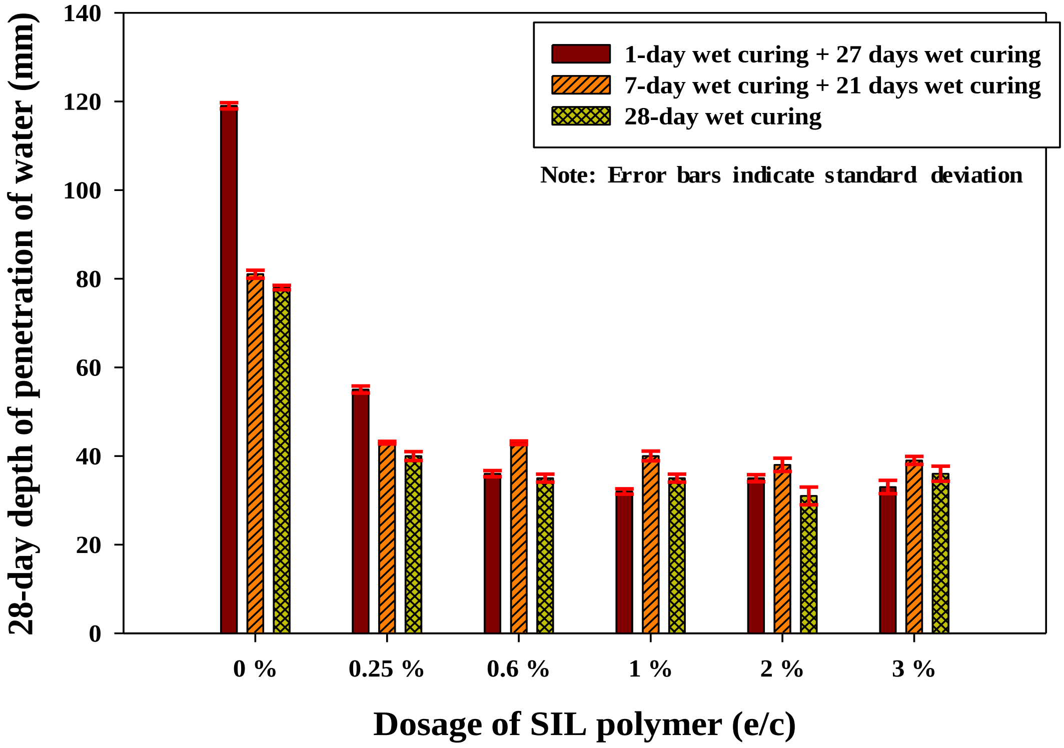


Figure 4.22: Water permeability of SIL PMMs at various curing types for dosages of 0.25 % to 3 % e/c

4.8 Discussion

From the study carried out to understand the influence of curing on the properties of PMMs, it can be seen that the performance depends significantly on the dosage and the type of curing. It is necessary to acknowledge suitability practices for different applications depending on the requirements.

The results of mechanical properties (compressive strength and flexural strength) indicate that the curing type influences the strength, with limited duration of wet curing (7 days) followed by air curing ensuring better mechanical performance in PMMs. In the case of silane modified mortars, the trend was similar to UCM with the strengths increasing with curing duration. In terms of shrinkage and water permeability, the polymeric systems with higher pore volume in the larger pore sizes (10 µm to 10 nm) showed an increase in water permeability and systems with higher pore volume in lower pore sizes (2 nm – 10 nm) showed higher shrinkage. Thus, a limited period (1 day and 7 days) of wet curing (i.e., Type 1 and Type 2) results in lower shrinkage in comparison with prolonged periods (28 days) of wet curing (i.e., Type 3), which was essential for better water permeability characteristics of the repair mortars. It was also noted that an increase of polymer dosage in PMMs could result in higher performance only when leaching is controlled, possibly due to which PAE systems failed to show improvement in properties with dosage.

The properties of PMMs was found to be highly dependent on curing more in the PAE than in SBR mortars; with the least impact on silane mortars. The morphological analysis done using SEM validates the findings of microstructure, which shows that the SBR and PAE mortars microstructure were affected by curing and silane had the least impact of the curing.

4.9 Summary

This chapter reports the results evaluating the influence of curing on the performance of PMMs after exposure to 28 days of various curing types (without any exposure to external environment conditions). The following table summarises the inferences drawn based on the test results.

Property	Inference
Fresh state properties (flow, wet density, setting times)	(i) Polymer modification in cementitious system resulted in improved workability, lower wet density, higher air entrainment and extended setting time. (ii) Among all PMMs tested, silane showed higher workability with lower decrease in wet density and setting time.
Shrinkage and water permeability	(i) Shrinkage strain of the polymeric systems was lower with limited durations of wet curing (1 to 7 days), whereas water permeability results improved with curing durations (28 days). (ii) SBR systems showed lower shrinkage and water permeability with the three types of curing at both dosages

Sensitivity to curing	(i) Performance of PAE was more sensitive to curing type than SBR and silane systems. Type 3 curing (i.e., 28 days of wet curing) resulted in poor results for PAE mortars in terms of shrinkage and water permeability; (ii) However, minimal effects were seen on SBR and silane mortar systems.
Effect of dosage	(i) At higher dosages (10 %), PAE gave higher shrinkage and increased the depth of water penetration. (ii) However, SBR modified mortars had lower shrinkage and reduced penetration of water.
Recommendations for specific properties	(i) Low shrinkage and water permeability: SBR at 10 % dosage. (ii) High mechanical properties: PAE systems at lower dosages (4.5 %).
Recommendations for specific polymers (for lower shrinkage and water permeability, and good mechanical properties)	(i) SBR – 10 % p/c 7-day wet curing followed by air curing (ii) PAE – 4.5 % p/c 7-day wet curing followed by air curing (iii) SIL – 0.25 % e/c 7-day wet curing followed by air curing

CHAPTER 5

PERFORMANCE EVALUATION OF PMMS AFTER EXPOSURE TO WEATHERING CONDITIONS

5.1 Introduction

Assessing the performance at possible critical conditions helps make suitable recommendations of the polymeric system for different applications. Most commonly used SBR polymers undergo cross-linking of the polymeric chains by photo-degradation due to exposure to UV. The cross-linking of polymeric chains decreases the viscosity of the pore solution and cause permeation in the gel due to photo-degradation. This brings about bulk changes in the mechanical properties (Noriman and Ismail 2011). Also, studies by Krishnan (2014) suggest that the usage of various polymeric systems can be recommended only after evaluation of the sensitivity of the properties to the exposure conditions that the functionality can offer. Thus, to understand the sensitivity of polymeric systems to such exposure conditions typical of exterior applications, such as waterproofing, overlays and repair, it is essential to understand the properties after weathering.

This chapter presents the results of tests done on various PMMs after accelerated weathering, with a cyclic exposure to UV and high humidity conditions. An extensive matrix of materials and experiments with the dosages and curing types are considered in the evaluation under accelerated environment. The performance of polymeric systems with ageing is also compared to that of UCM to assess the sensitivity of these systems under such exposure.

5.2 Engineering properties of PMMs after exposure to accelerated weathering

After 28 days of age under different types of the curing, the mortars were subjected to 30 days of exposure to accelerated weathering (see Section 3.6), after which the compressive and flexural strengths have been evaluated and reported in this section.

5.2.1 Compressive strength

The mean compressive strengths at various dosages and curing types after exposure to accelerated conditions of weathering are reported in Table 5.1 and Figure5.1.

Table 5.1: Mean compressive strengths (and standard deviations) of UCM and PMMs tested after accelerated weathering

Type of mortar	Dosage	Mean compressive strength (MPa)		
		1 day wet curing	7 days wet curing	28 days wet curing
UCM	0 % p/c	49.0 (±0.1)	50.7 (±3.0)	60.9 (±2.1)
SBR	4.5 % p/c	25.3 (±2.5)	29.7 (±1.2)	35.0 (±0.6)
	10 % p/c	24.8 (±0.6)	22.5 (±0.5)	31.0 (±0.8)
PAE	4.5 % p/c	27.4 (± 1.4)	38.3 (±0.6)	45.0 (±1.2)
	10 % p/c	22.6 (± 0.8)	28.9 (±0.9)	30.6 (±0.9)
SIL	0.25 % e/c	46.7 (±2.0)	50.7 (±3.2)	53.3 (±1)

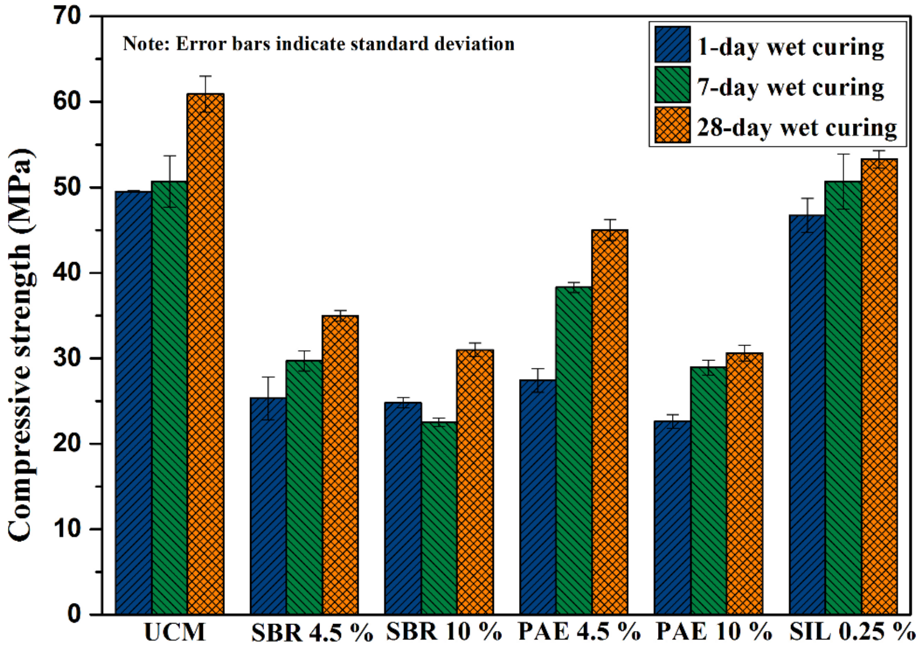


Figure5.1: Mean compressive strengths of UCM and PMMs at various curing types after accelerated weathering conditions

After exposure to accelerated conditions of weathering, the strength of PMMs was higher for the specimens that had undergone longer periods of wet curing (28 days).

From SEM images (Figure 4.3), it was seen that polymer film formation occurs more with limited duration of wet curing rather than in longer wet curing periods, which could explain the lower degradation of strength.

Table 5.2: Change in compressive strength of mortar after accelerated weathering

Type of mortar	% change in compressive strength of mortars after accelerated weathering		
	1 day wet curing	7 days wet curing	28 days wet curing
UCM	86.3	-1.46	13.2
SBR 4.5 %	-14.8	-13.2	15.5
SBR 10 %	-5.7	-12.1	32.5
PAE 4.5 %	-4.2	0.3	14.5
PAE 10 %	0	6.3	30.2
SIL 0.25 %	69.8	49.5	41.0

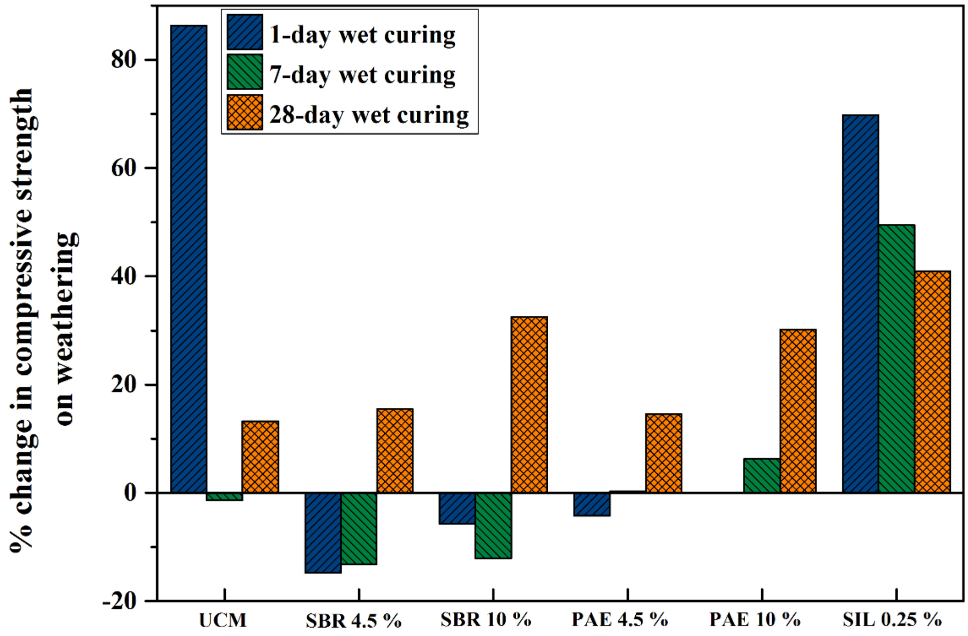


Figure5.2: Change in compressive strength of various mortars after weathering

In Table 5.2 and Figure5.2, the change in compressive strength on weathering with respect to the corresponding unweathered (at 28 days) value for each curing type and dosage, is presented. For example, 22.7 % is the increase in compressive strength of UCM after exposure to weathering conditions (i.e., 26.3 MPa strength at 28 days after curing, before exposure to weathering and 49 MPa after exposure to weathering conditions). The compressive strengths of the UCM and silane mortars were not affected by weathering, and even showed an increase. PAE systems with limited wet curing (1 to 7 days) retained the strength while specimens with longer wet curing periods (28 days) showed an increase in compressive strength. Reduction in strength was higher in SBR mortars at all dosages with a limited period of curing. All polymeric specimens showed an improvement in strength with longer periods of wet curing (28-day curing), irrespective of the polymer type and dosages used. The lower strength noted on exposure to accelerated weathering for systems with limited wet curing is on the account of the polymer film deterioration in the PMMs; whereas the system with extended wet curing periods had lesser impact due to polymer modifications, which helps to retain higher strength. This indicates that a reduction in strength should be expected and considered for polymeric systems in applications with such exposure conditions. The polymer film in the silane mortar systems had less deterioration due to moisture and UV exposure (Moradllo et al. 2013), which results in a progressive increase in strength in all curing types. Only silane mortars showed an increase in compressive strength other than UCM, independent of the curing types.

Table 5.3: Change in compressive strength of the PMMs after weathering compared to the weathered UCM

Type of mortar	% change in compressive strength of the PMMs to the UCM after accelerated weathering (MPa)		
	1 day wet curing	7 days wet curing	28 days wet curing
SBR 4.5 % p/c	-48.4	-41.4	-42.5
SBR 10 % p/c	-49.3	-55.6	-49.1
PAE 4.5 % p/c	-44.1	-24.5	-26.1
PAE 10 % p/c	-53.8	-42.9	-49.7
SIL 0.25 % e/c	-4.7	0	-12.5

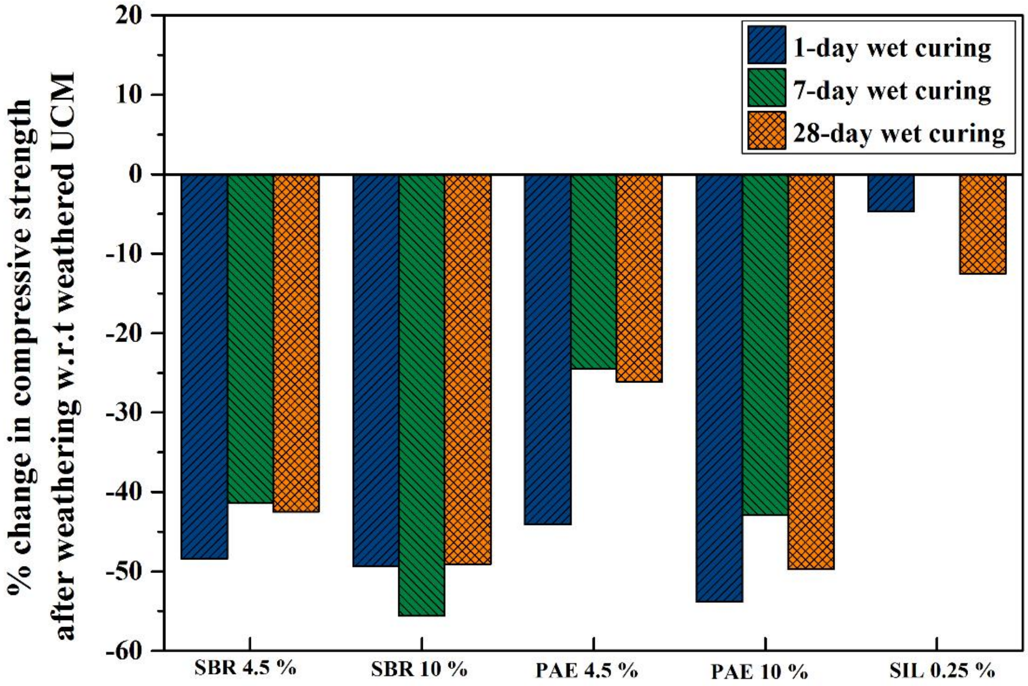


Figure 5.3: Change in compressive strength of PMMs to the UCM at various curing conditions after accelerated weathering

The comparison of the performance of weathered PMMs with the weathered UCM (see Figure 5.3 and Table 5.3), showed that polymer additions can result in lower compressive strength due to weathering when compared to an unmodified mortar. Except for the silane systems with 1- and 7- day curing, other systems suffered a large decrease in strength relative to the UCM on weathering. This decrease was found to be more at higher dosages (10 %) of polymers, especially when wet cured for 1 day.

5.2.2 Flexural strength

The flexural strengths of PMMs subjected to various curing conditions after exposure to accelerated conditions of weathering are given in Table 5.4 and Figure 5.4. From the flexural strengths of UCM and PMMs, with various curing types (Figure 5.4), the value with 28-day wet curing were higher, as in the trends seen in compressive strength. However, the performance of silane mortars for different curing types was similar.

Table 5.4: Mean flexural strength of UCM and PMMs for different curing conditions tested after accelerated weathering (and standard deviation).

Type of mortar	Dosage	Flexural strength (MPa)		
		1 day wet curing	7 day wet curing	28 day wet curing
UCM	0 % p/c	4.2 (±1.7)	7.3 (±0.9)	7.6 (±1.1)
SBR	4.5 % p/c	7.3 (±0.3)	7.3 (±0.3)	9.2 (±0.8)
	10 % p/c	8.1 (±0.8)	7.7(±0.4)	9.6 (±0.6)
PAE	4.5 % p/c	4.2 (±1.2)	4.7 (±0.6)	4.9 (±0.4)
	10 % p/c	4 (±0.9)	4.2 (±1.3)	4.5 (±0.6)
SIL	0.25 % e/c	7.1 (± 0.6)	6.9 (±0.2)	7.0 (±0.6)

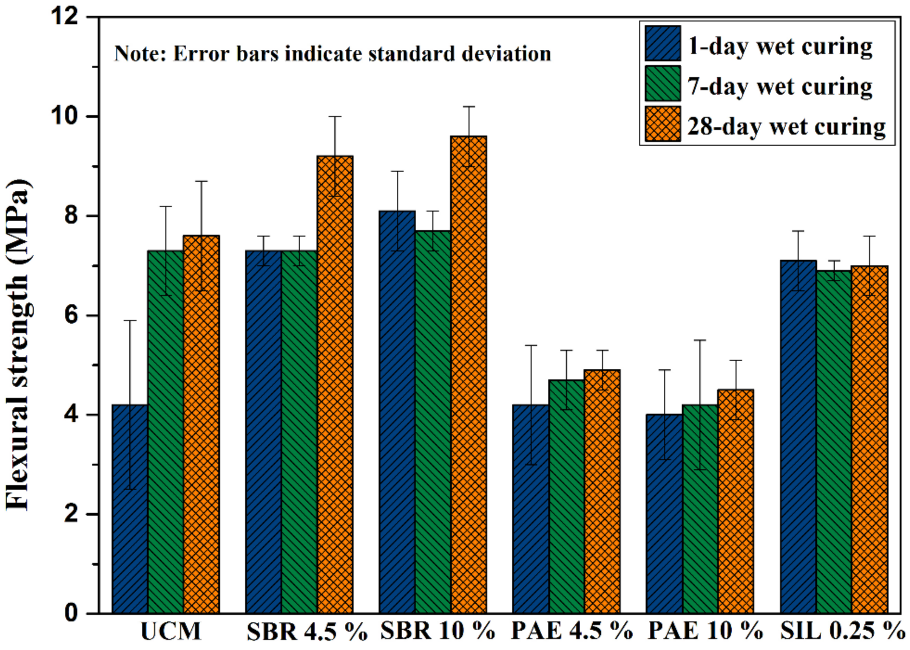


Figure 5.4: Mean flexural strengths of UCM and PMMs with various curing types after accelerated weathering

The SBR and silane polymeric systems showed an increase in flexural strength on ageing, for all curing types (Table 5.5 and Figure 5.5). This is in contradiction to literature that suggests that the SBR polymeric systems lose tensile strength when subjected to UV exposures (Noriman and Ismail 2011). The PAE systems suffered a loss in the flexural strength at all dosages and curing conditions. Generally, the positive effects of PAE addition occurs with age due to a delay in polymer film formation (Ramli et al. 2013) that may not have happened here due to the accelerated weathering. Thus, an early exposure of the acrylic polymeric system to exterior environments could hamper their performance in practice. It also appears that in polymeric systems, aging can lead to a greater reduction in flexural strength than compressive strength as the polymeric additions, in general, have a greater influence in flexure than in compression, thereby making the flexural strength more affected by the disruption of polymeric interaction in a PMM.

Table 5.5: Change in flexural strength of mortars after accelerated weathering

Type of mortar	% change in flexural strength of mortars after accelerated weathering		
	1 day wet curing	7 days wet curing	28 days wet curing
UCM	-26.3	14.1	5.6
SBR 4.5 %	55.3	46	76.9
SBR 10 %	52.8	57.1	104.3
PAE 4.5 %	-33.3	-35.6	-21.0
PAE 10 %	-24.5	-14.3	-4.26
SIL 0.25 %	10.9	0	2.9

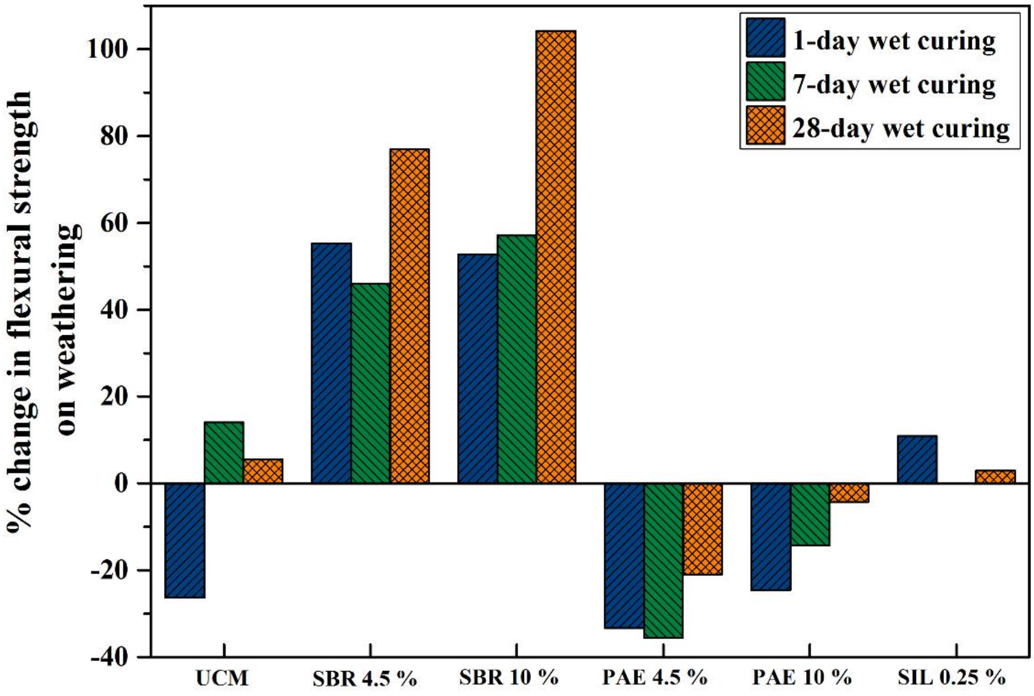


Figure 5.5: Change in flexural strength of various mortars after accelerated weathering

Table 5.6 and Figure 5.6 shows the comparison of the flexural strengths of various polymeric systems on aging with the reference to the weathered UCM mortar. All polymeric systems except PAE show comparable performance to the reference mortars, indicating an improvement or better retention of flexural strength in these systems. The loss of flexural strength on weathering was found to be higher with an increase in dosage levels of PAE polymer. From these results, it is understood that acrylic polymeric systems, which have a higher interaction at lower dosages, give better performance with aging.

Table 5.6: Change in flexural strengths of PMMs after accelerated weathering when compared to the weathered UCM

Type of mortar	% change in flexural strength of the PMMs to the UCM after accelerated weathering		
	1 day wet curing	7 days wet curing	28 days wet curing
SBR 4.5 % p/c	73.8	0	21
SBR 10 % p/c	45.9	5.5	26.3
PAE 4.5 % p/c	0	-35.6	-35.5
PAE 10 % p/c	-4.7	-42.5	-40.8
SIL 0.25 % e/c	69.0	-5.5	-7.9

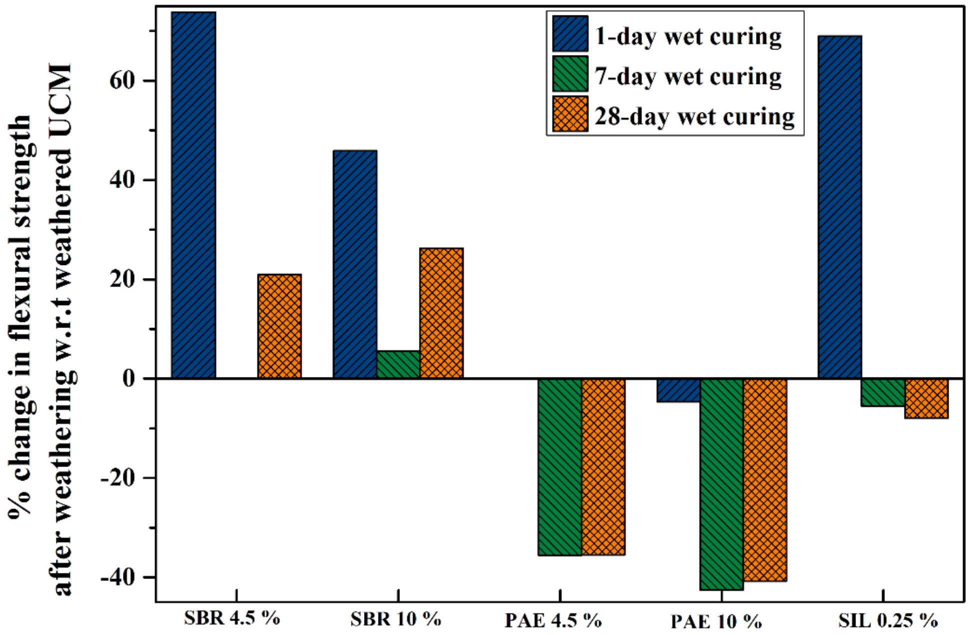


Figure 5.6: Change in flexural strength of various PMMs to the UCM after accelerated weathering conditions

5.3 Total drying shrinkage

The shrinkage strain measured in PMMs and UCM after various curing conditions and exposure to accelerated conditions of weathering is given in Table 5.7. The shrinkage of the mortars when subjected to drying after the accelerated weathering was higher for specimens with 28-day wet curing. Hence, the possible approach of longer curing of polymeric systems for exteriors could result in a higher shrinkage.

Table 5.7: Total drying shrinkage of PMMs and UCM at various curing types after exposure to accelerated weathering

Type of mortar	Dosage	Total drying shrinkage (micro strain)		
		1 day wet curing	7 days wet curing	28 days wet curing
UCM	0 % p/c	181	158	163
SBR	4.5 % p/c	182	207	379
	10.0 % p/c	221	249	305
PAE	4.5 % p/c	413	300	636
	10.0 % p/c	232	535	736
SIL	0.25 % e/c	166	222	241

Table 5.8 and Figure 5.7, the shrinkage strains of PMMs were lower with aging than the shrinkage strain obtained after 28 days. Since, the drying shrinkage of mortars depends on the loss of water from the cementitious systems (Thomas et al. 2017), lower moisture loss is expected at later ages, resulting in lower shrinkage. This shows that the effect of aging was found to have lower influence on shrinkage for all polymeric systems, and the shrinkage strains after exposure to accelerated weathering were lower than those before exposure to such conditions.

Table 5.8: Change in shrinkage of mortars after accelerated weathering

Type of mortar	% change in shrinkage strain of mortars after accelerated weathering		
	1 day wet curing	7 days wet curing	28 days wet curing
UCM p/c	-59.7	-64	-69.6
SBR 4.5 % p/c	-59.7	-4.4	-36.5
SBR 10 % p/c	-40.6	-4.8	-57.5
PAE 4.5 % p/c	-73.3	-64.7	-23
PAE 10 % p/c	-69.5	-45.7	-41.4
SIL 0.25 % e/c	-73.2	-73.3	-55.4

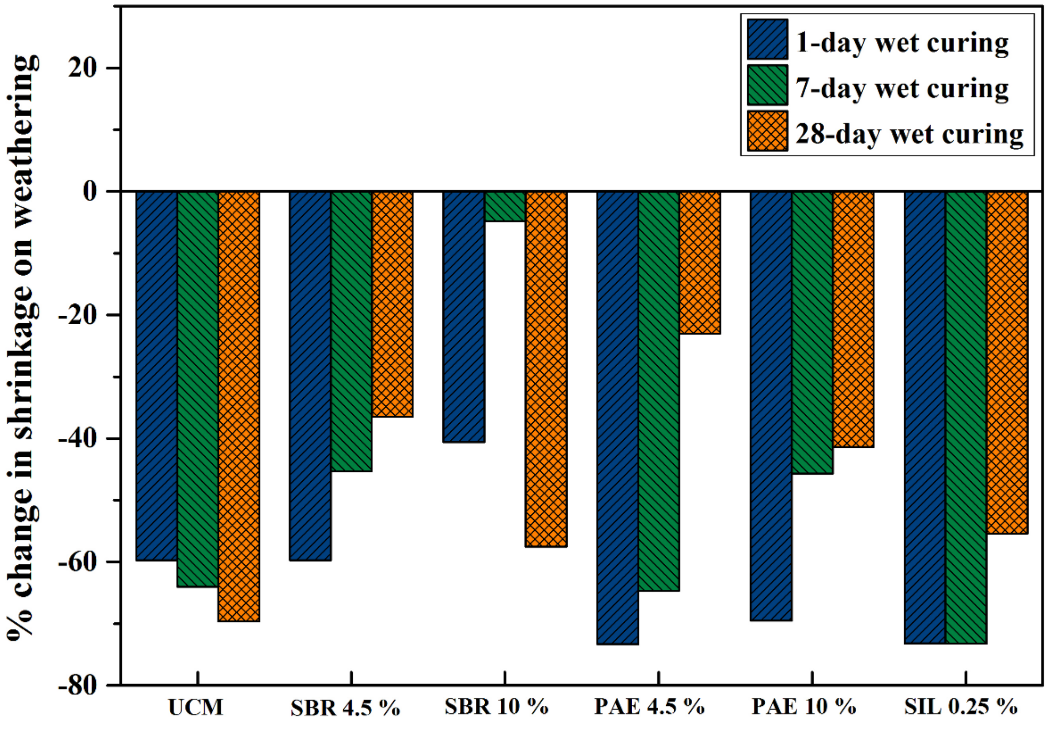


Figure 5.7: Change in shrinkage strain of various mortars after accelerated weathering

It was also noted that the shrinkage of all PMMs subjected to weathering was higher than the UCM exposed to similar conditions, except for silane mortars subjected to Type 1 curing (Table 5.9 and Figure 5.8). Higher increase in shrinkage is seen in mortars subjected to longer wet curing periods (e.g., Type 3) than for Type 1 and Type 2 curing. Thus, the positive effects of polymer addition for shrinkage properties were not seen with the conventional polymeric systems of SBR and PAE. However, a lower relative increase in shrinkage was observed in SBR mortars with all curing types than in the PAE mortars.

Table 5.9: Change in shrinkage of the PMMs after accelerated weathering when compared to the weathered UCM

Type of mortar	% change in shrinkage strain of the PMMs to the UCM after accelerated weathering		
	1 day wet curing	7 days wet curing	28 days wet curing
SBR 4.5 % p/c	0.6	31	132
SBR 10 % p/c	22	57.5	87
PAE 4.5 % p/c	128	89.8	290
PAE 10 % p/c	28	238	351
SIL 0.25 % e/c	-8.3	40.5	47.8

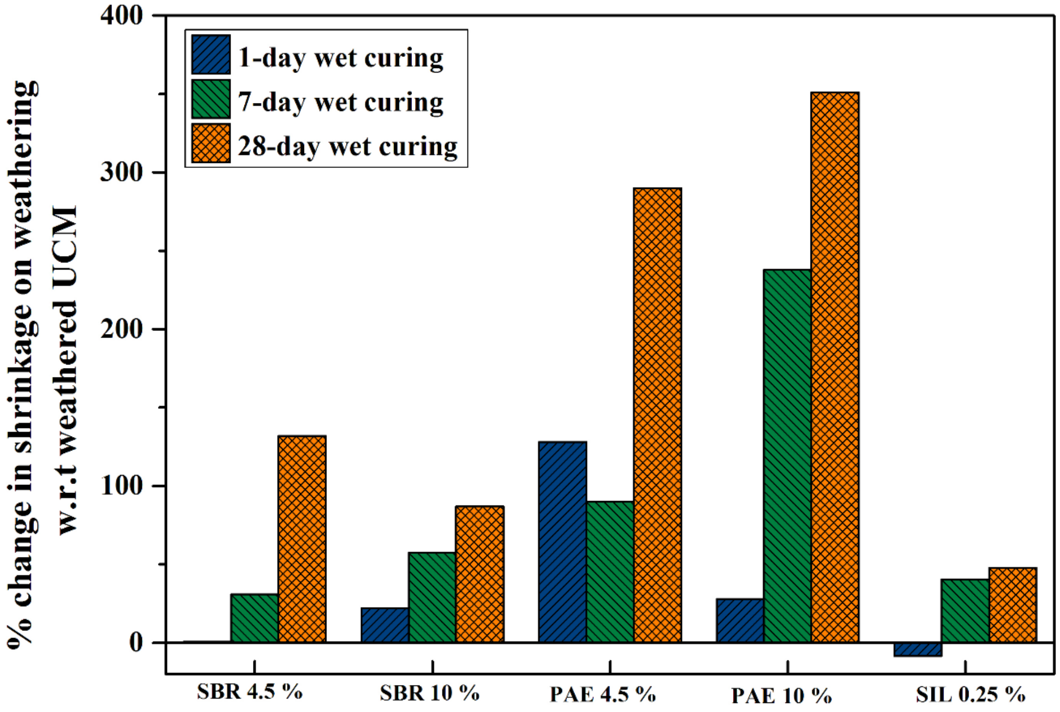


Figure 5.8: Change in shrinkage strain of various PMMs to the UCM after accelerated weathering

5.4 Water permeability

Water permeability results of the PMMs after exposure to accelerated conditions of weathering are presented in Table 5.10 and Figure 5.9. In general, permeability of all PMMs was found to be higher than UCM after exposure to accelerated weathering.

Among the PMMs, SBR and silane suffered lower penetration of water. It was also noted that the water permeability was similar for silane mortars at all curing conditions, in contrast with other polymeric systems, which seem to be sensitive to the curing type.

Table 5.10: Penetration of water of PMMs and UCM at various curing conditions after accelerated weathering

Type of mortar	Dosage	Depth of penetration of water (mm)		
		1 day wet curing	7 days wet curing	28 days wet curing
UCM	0 %	49	18	7
SBR	4.5 %	99	40	20
	10 %	150	115	151
PAE	4.5 %	93	82	120
	10 %	128	53	52
SIL	0.25 %	62	70	65

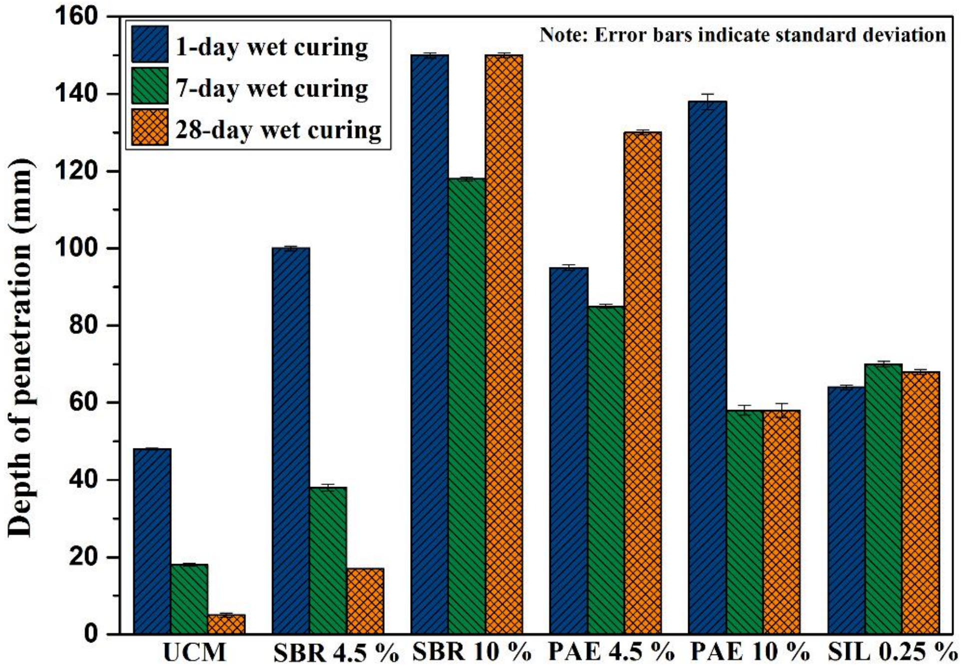


Figure 5.9: Water permeability results of PMMs at various curing types after exposure to accelerated weathering

As seen from Table 5.11 and Figure 5.10, the PAE and silane mortars have lower penetration of water after accelerated weathering, at all dosages and curing conditions, signifying an improvement in performance with the exposure. SBR modified systems showed an increase in water permeability after exposure to accelerated weathering suggesting a deterioration of these systems in exterior applications.

Table 5.11: Change in penetration of water of PMMs and UCM after accelerated weathering

Type of mortar	Dosage	% change in depth of penetration of water of mortars after accelerated weathering		
		1 day wet curing	7 days wet curing	28 days wet curing
UCM	0 %	-58.3	-77.7	-91
SBR	4.5 %	70.6	122.2	25
	10.0 %	294	576.4	843.8
PAE	4.5 %	-33.6	-42.6	-20
	10.0 %	1.6	-61.6	-57
SIL	0.25 %	-47.5	-49.6	-44.9

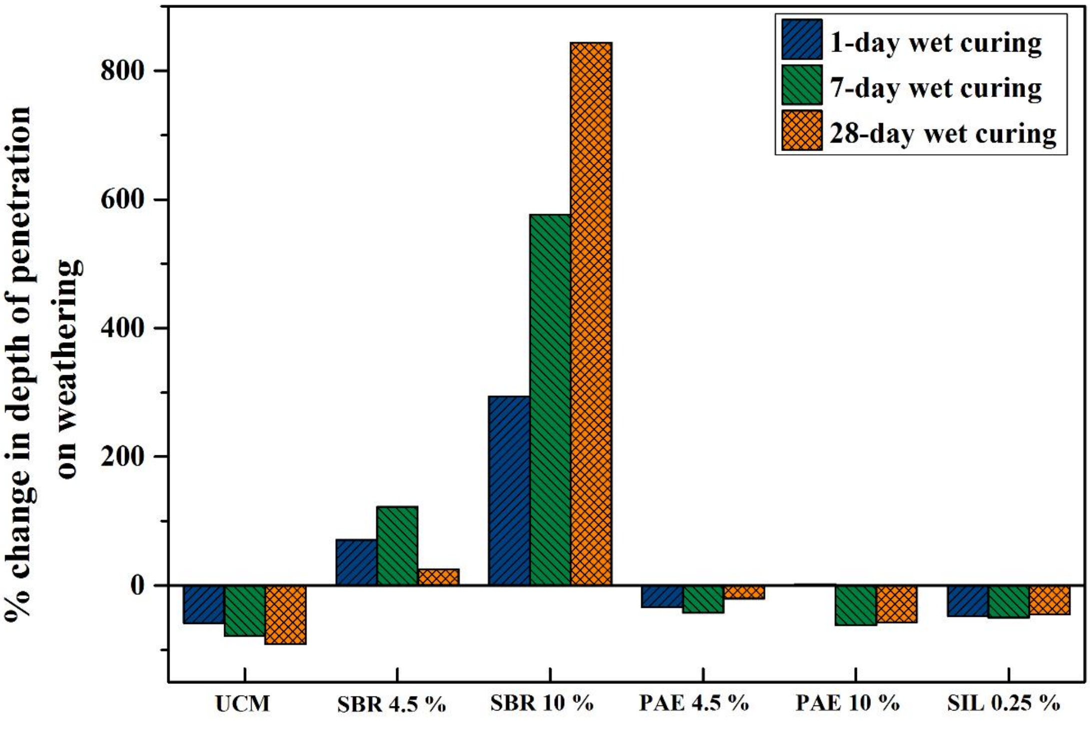


Figure 5.10: Change in water permeability of various PMMs after exposure to accelerated conditions of weathering

The performance of PMMs on weathering showed a relative increase in water permeability than the UCM for the different dosages and curing types (as shown in Table 5.12 and Figure 5.11). The usage of SBR modified systems needs to be carefully decided for applications of waterproofing requirement as higher dosages of SBR polymer results in lower permeability resistance.

Table 5.12: Change in the depth of penetration of water of PMMs on accelerated weathering when compared to weathered UCM

Type of mortar	Dosage	% change in depth of penetration of water of PMMs to weathered UCM after accelerated weathering		
		1 day wet curing	7 days wet curing	28 days wet curing
SBR	4.5 %	102	122	185
	10.0 %	206	538	2057
PAE	4.5 %	89	355	1614
	10.0 %	161	194	642
SIL	0.25 %	26.5	288	828

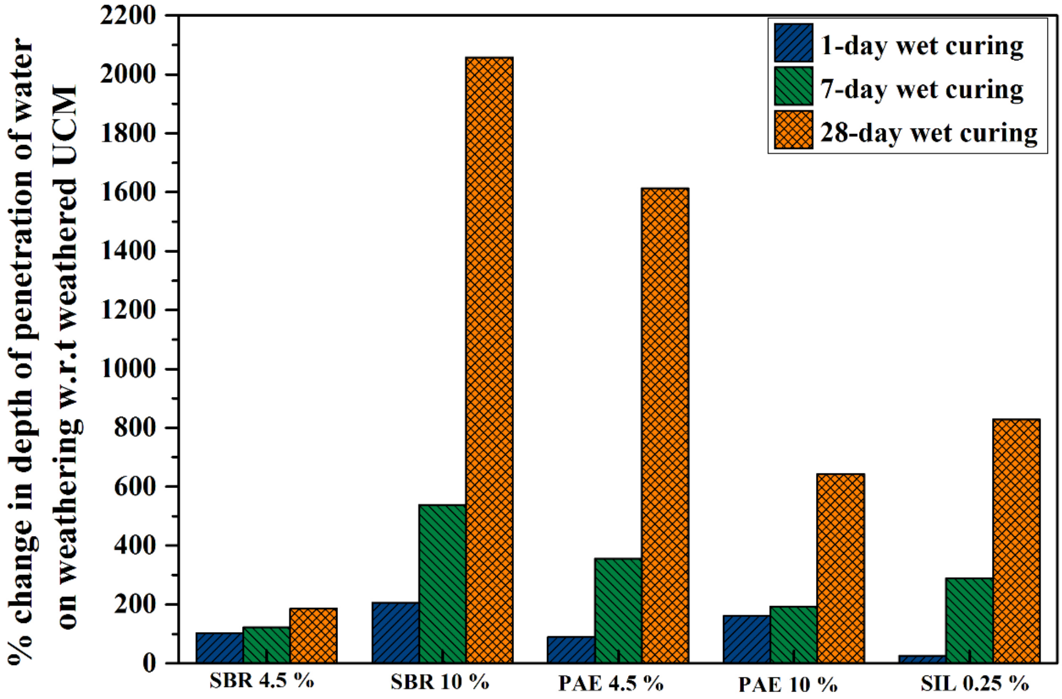


Figure 5.11: Change in water permeability of various PMMs after accelerated weathering to weathered UCM

5.5 Effect of dosage of SIL polymers on performance of SIL PMMs

This section discusses the properties of silane polymeric systems after subjected to weathering and the influence of dosage. The mortars were cast with the SIL e/c ratios of 0.25 %, 0.6 %, 1 %, 2 % and 3 %, and tested for mechanical properties and water permeability.

From the mechanical properties obtained for SIL PMMs tested at various dosages after weathering (Figure 5.12 and Figure 5.13), it was seen that dosages greater than 1 % resulted in a marginal decrease in strength than the lower dosages. For compressive strength, higher values were observed with longer moist curing (28-day wet curing), while for flexural strengths 28-day wet curing resulted in higher flexural strengths for e/c lesser than 1 %, and 1-day wet curing favoured dosages greater than 1 %.

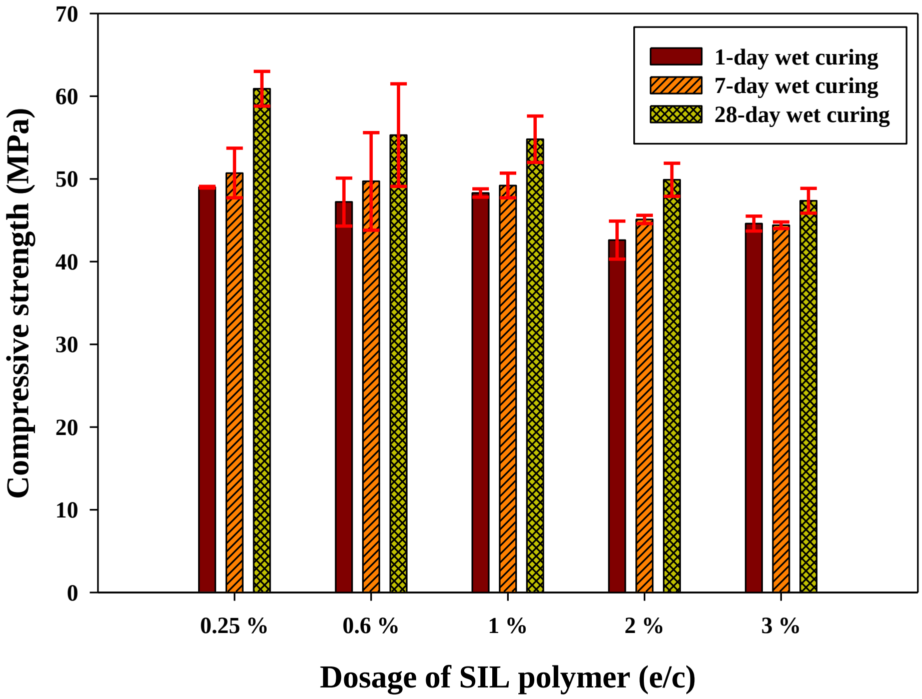


Figure 5.12: Compressive strength results of SIL PMMs at various curing types for dosages from 0.25 % - 3 % e/c after accelerated weathering

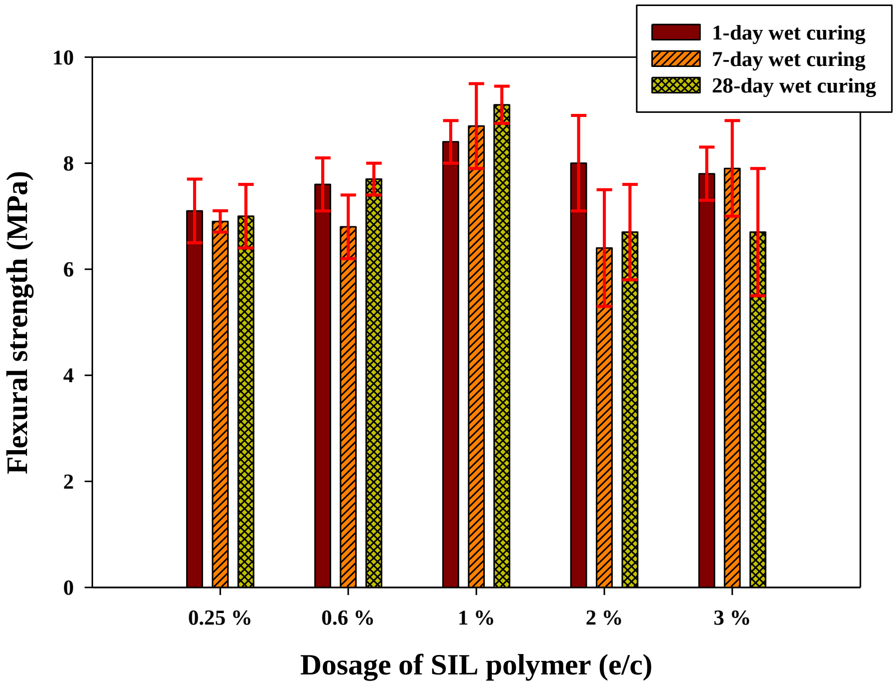


Figure 5.13: Flexural strength results of SIL PMMs at various curing types for dosages from 0.25 % - 3 % e/c after accelerated weathering

From the water permeability results of SIL mortars as plotted in Figure 5.14, the depth of penetration of water into the silane mortar systems remained less affected by weathering with no reduction in performance on exposure to weathering. The high stability of Si-O bonds present in silanes makes them less susceptible to UV radiations, ensuring a low depth of penetration of water, even when tested for higher dosage levels greater than 1 %.

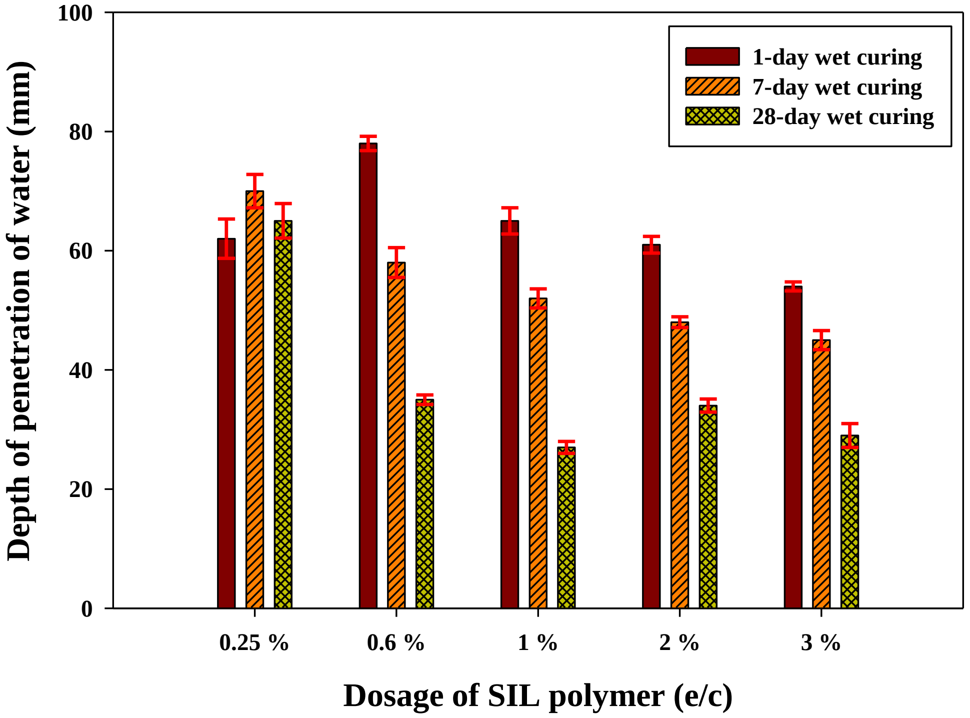


Figure 5.14: Water permeability results of SIL PMMs at various curing types for dosages from 0.25 % - 3 % e/c after accelerated weathering

Thus, for outdoor applications, considering cost and performance, dosages of 1 % with 28-day wet curing can be recommended. However, it should be understood that the enhancements achieved in terms of an increase in dosage is marginal and may not compensate the costs involved.

5.6 Discussion

From the test results, it is inferred that the performance of the polymeric systems could largely depend on the type of exposure conditions. It was also understood that the performance of UCM and PMMs on aging can be differentiated mainly due to the variations in the polymers present in these systems. Silane mortars show less dependence on curing and exposure among other PMMs tested, making them suitable for outdoor applications.

The silane polymeric systems had higher stability to accelerated weathering than the other polymers tested, due to the Si-O-Si bonds. This is because the energy of the UV wavelengths (below 290 nm) is sufficient to break bonds of C-O, C-C, C-H and C-N present in common polymeric systems. However, a more stable Si-O-Si bonds in silanes imparts higher resistance to UV exposure, and therefore, there is better retention of properties after exposure to accelerated weathering (Materne et al. 2012).

Among the curing types, it was seen that limited wet curing periods, which can cause more effective polymer film formation, could lead to lower retention of mechanical and durability properties upon exposure to weathering conditions. Longer period of wet curing periods resulted in better retention of strengths and permeability for all curing types and dosages.

5.7 Summary

This chapter discusses the performance of PMMs on exposure to accelerated weathering and the sensitivity of the polymeric systems to such exposure conditions. Specifically, the following conclusions have been drawn.

(i) With respect to exposure to exterior environments, PMMs were found to be more susceptible to aging conditions than the UCM.

(ii) Extended period of wet curing (28 days) showed better mechanical properties and durability than shorter wet curing periods (1 days and 7 days).

(iii) Silane modified systems showed improvement in all the properties evaluated after exposure to accelerated weathering. Such good retenion of properties on aging is mainly due to the highly stable Si-O-Si bond in SIL polymers.

(iv) Ageing was found to impact polymer additions positively only for silane mortars subjected to shorter periods of wet curing of 1-day. All other polymeric systems showed a loss of properties on exposure to accelerated weathering when compared to the unmodified mortar subjected to similar conditions of aging.

(v) Among the conventional polymeric systems, except for the flexural strength, PAE mortars showed more retention of performance than the SBR systems, making PAE mortars more apt for exterior applications.

(vi) Based on the assessment made in this Chapter, the following recommendations are given for the outdoor applications of PMMs (in terms of specific properties), where weathering is expected to occur (see Table 5.13).

Table 5.13: Recommendations for mortars subjected to weathering in outdoor applications in terms of the requirement for specific properties

Property that is critical in the application	Recommended dosage and curing for higher retention of properties on aging	Recommended dosage and curing for higher retention of properties on aging w.r.t UCM
Compressive strength	SIL 0.25 % 28-day wet curing	SIL 0.25 % 7-day wet curing
Flexural strength	SBR 10 % 28-day wet curing	SBR 10 % 1-day wet curing
Drying shrinkage	SIL 0.25 % 1-day wet curing	SIL 0.25 % 1-day wet curing
Water permeability	SBR 4.5 % 28-day wet curing	SIL 0.25 % 1-day wet curing

CHAPTER 6

PERFORMANCE EVALUATION OF PMMS AT ELEVATED TEMPERATURES

6.1 Introduction

Polymeric systems are used for applications such as repair mortars and waterproofing. Such applications of polymeric systems make them susceptible to damage on exposure to high temperature say, in a fire. In order to ensure the safe functionality of these systems during and after fire, it becomes necessary to evaluate the performance of polymeric systems at elevated temperatures for considering the reduced strength and properties in design.

In this chapter, the performance of PMMs with SBR, PAE and SIL at a range of elevated temperatures from 100 °C to 600 °C are presented. The retention of compressive and flexural strengths was assessed after exposure. The porosity and pore size distribution of the polymeric systems after exposure to high temperature were also evaluated.

6.2 Experimental procedures

Mortar specimens were cast for the evaluation of compressive (50 mm cubes) and flexural (160 mm × 40 mm × 40 mm) strengths and subjected to 28 days of wet curing. In this study, PAE and SBR mortar samples with 10 % dosages were subjected to elevated temperature. For silanes, an emulsion-cement ratio of 0.25 % was adopted. The specimens were heated, after 28 days of curing, in a muffle furnace, where they were subjected to various temperatures from 100 °C to 600 °C, at a heating rate of 5 °C/minute approximately. At each temperature condition, the specimen was held for a period of 1 hour, after which they were cooled to room temperature at a rate of approximately 3 °C/minute. The specimens were removed from the furnace and tested for the retention of the relevant property after exposure. A sample (~ 0.8 grams) was collected from the centre of the specimen for porosity evaluation, and conditioned for 4 days in isopropanol and dried in vacuum. Figure 6.1 shows an inside view of the muffle furnace during the high temperature.

Figure 6.1: Specimens subjected to high temperature conditions in muffle furnace.

6.3 Experimental results on mechanical properties

The compressive and flexural strengths retained at each of the elevated temperatures are reported in this section.

6.3.1 Compressive strength

The residual compressive strengths of each PMM, along with the results of unmodified cementitious system, are presented in Table 6.1 and Figure 6.2. It was clear that incorporation of polymers reduces the strength, indicated by the lower values in comparison to the UCMs. The compressive strength of UCM showed a marginal increase when exposed to temperature up to 400 °C and a subsequent reduction when heated further. The initial increase can be a result of hydration of the unhydrated cement grains at these elevated temperatures and the decrease thereafter on the account of decomposition of $Ca(OH)_2$ occurring above 400 °C (Muthadhi and Kontharaman 2014).

The PMMs exhibit an initial decrease in the compressive strength when heated to 100 °C followed by an increase in strength at 200 °C. The SBR modified mortar experienced a more pronounced increase in strength at 100 °C. Above 300 °C, the strength continuously reduced, as seen from Figure 6.2. The drastic fall in strength of PMMs could be attributed to the deterioration of polymers above the transition temperature, resulting in internal stresses and generation of microcracks. On the contrary, silane modified mortars behaved almost as an unmodified mortar would with no sharp decrease in strength even when exposed to temperatures up to 500 °C. Among the PMMs, silane modified systems showed higher retention of compressive strength at elevated temperature.

Table 6.1: Compressive strength results of UCM and PMMs after exposure to elevated temperatures (and standard deviation)

Temperature (°C)	Mortar system	Compressive strength (MPa)	% change in compressive strength
Room temperature	UCM	45.4 (±0.5)	-
	SBR 10 % p/c	25.0 (±0.8)	-
	PAE 10 % p/c	23.5 (±0.8)	-
	SIL 0.25 % e/c	46.2 (±3.2)	-
100	UCM	45.6 (±4.6)	0.4
	SBR 10 % p/c	29.0 (±0.3)	16
	PAE 10 % p/c	22.5 (±2.3)	-4.3
	SIL 0.25 % e/c	43.1 (±1.6)	-6.7
200	UCM	47.1 (±1.9)	3.7
	SBR 10 % p/c	32.0 (±0.8)	28
	PAE 10 % p/c	24.8 (±1.9)	5.5
	SIL 0.25 % e/c	42.1 (±4.8)	-8.9
300	UCM	46.0 (±6 2)	1.3
	SBR 10 % p/c	29.0 (±4.4)	16
	PAE 10 % p/c	18.6 (±3.5)	-20.9
	SIL 0.25 % e/c	46.7 (±3.3)	1.1
400	UCM	47.0 (±0.8)	3.5
	SBR 10 % p/c	18.0 (±3.1)	-28
	PAE 10 % p/c	13.9 (±1.4)	-40.9
	SIL 0.25 % e/c	45.1 (±2.2)	-2.4
500	UCM	36.3 (±1.1)	-20
	SBR 10 % p/c	14.7 (±1.5)	-41.2
	PAE 10 % p/c	9.8 (±1.3)	-58.3
	SIL 0.25 % e/c	43.2 (±3.2)	-6.5

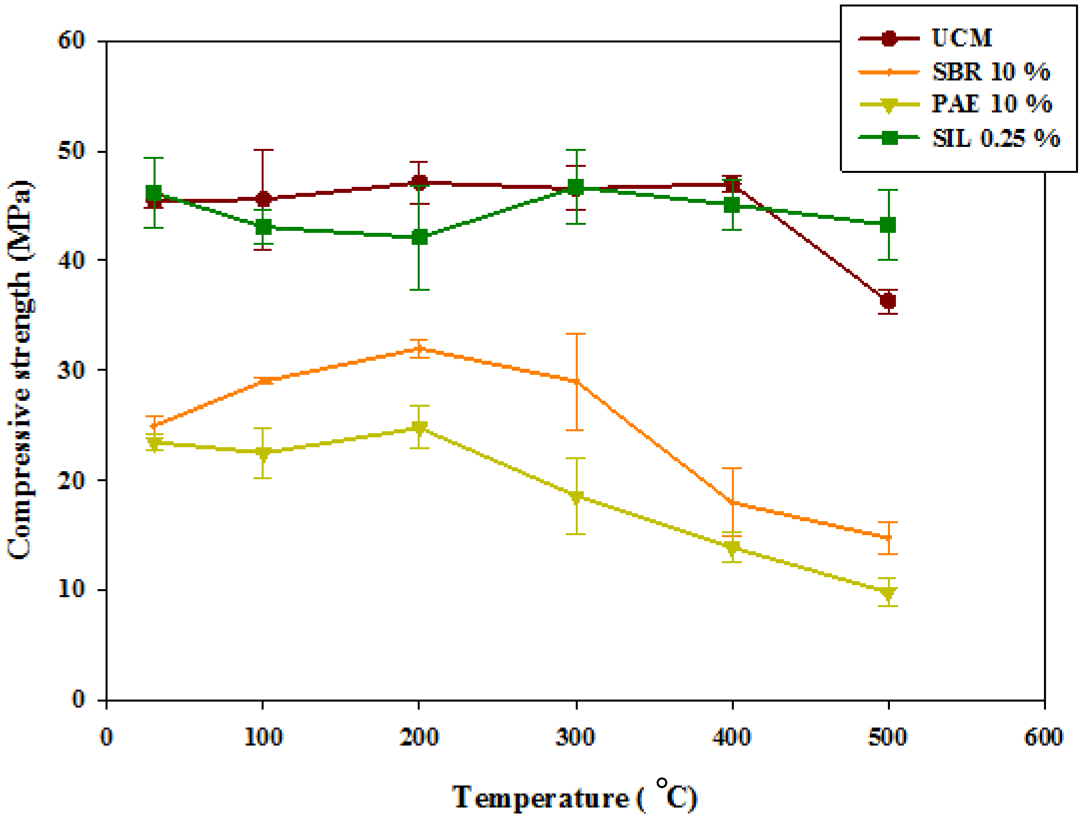


Figure 6.2: Mean compressive strength of the PMMs and UCM at elevated temperature.

The UCM and silanes retained about 80 % of the strength obtained at laboratory conditions (~27 °C) even at higher exposure temperature in excess of 400 °C, whereas SBR modified mortars retained about 60 % of strength, and PAE modified mortars 40 % of the strength. Thus, to account for the reduction in strength at elevated temperature in polymeric systems, a higher strength mortar is to be considered in design when conditions are expected to exceed 300 °C (for SBR) and 200 °C (for PAE) at the ultimate strength limit state. A factor of safety of 2 can be considered for SBR systems, 3.3 for PAE and 1.4 for SIL systems when exposed to temperatures greater than 400 °C.

6.3.2 Flexural strength

The results of flexural tests indicate a significant improvement in flexural strength values, for all PMMs except silanes, on exposure to temperatures up to 300 °C (Table 6.2 and Figure 6.3). However, above this temperature there was an evident loss of strength. The flexural strength of UCM was not significantly influenced by temperature up to 400 °C, above which, there was a reduction in the strength, and for silane modified mortars, a marginal decrease in strength was seen with the increase in temperature with a higher retention than the other PMMs even at 500 °C.

Table 6.2: Flexural strengths of UCM and PMMs after subjected to elevated temperatures (and standard deviation)

Temperature (°C)	Mortar system	Flexural strength (MPa)	% change in flexural strength
Room temperature	UCM	9.0 (±0.8)	-
	SBR 10 % p/c	4.7 (±0.7)	-
	PAE 10 % p/c	4.7 (±0.9)	-
	SIL 0.25 % e/c	6.8 (±0.2)	-
100	UCM	9.0 (±2.3)	0
	SBR 10 % p/c	4.6 (±1.8)	-2.1
	PAE 10 % p/c	6.8 (±1.2)	44.7
	SIL 0.25 % e/c	6.5 (±0.9)	-4.4
200	UCM	8.9 (±1.8)	-1.1
	SBR 10 % p/c	6.2 (±1.3)	31.9
	PAE 10 % p/c	5.4 (±2.6)	14.9
	SIL 0.25 % e/c	6.3 (±1.3)	-7.4
300	UCM	9.1(±1.2)	1.1
	SBR 10 % p/c	6.2 (±2.9)	31.9
	PAE 10 % p/c	4.9 (±3.3)	4.3
	SIL 0.25 % e/c	5.8 (±1.7)	-14.7
400	UCM	9.1 (±1.6)	1.1
	SBR 10 % p/c	2.8 (±1.9)	-40.4
	PAE 10 % p/c	3.5 (±1.5)	-25.5
	SIL 0.25 % e/c	5.1 (±0.6)	-25.0
500	UCM	8.0 (±2.2)	-11.1
	SBR 10 % p/c	1.3 (±2.3)	-72.3
	PAE 10 %p/c	1.8 (±1.1)	-61.7
	SIL 0.25 %e/c	4.9 (±0.4)	-27.9

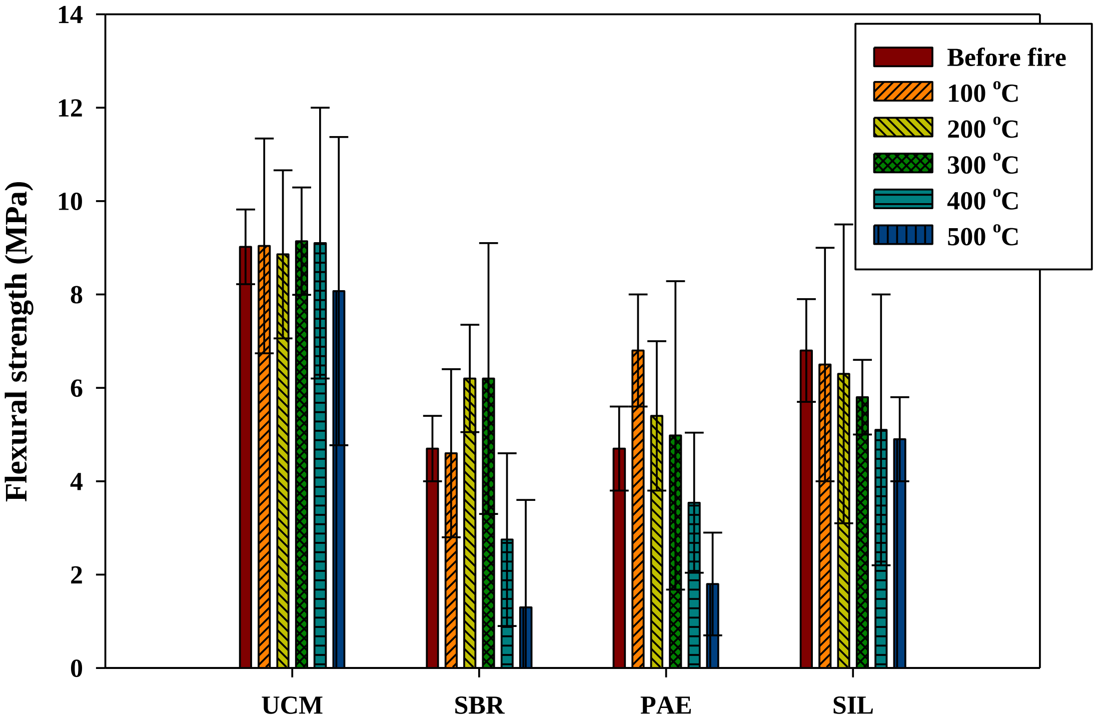


Figure 6.3: Mean flexural strength of the PMMs and UCM at elevated temperatures.

It was seen that more than 50 % of flexural strength was retained at even 400 °C for both SBR and PAE mortars and about 70 % was retained for silanes. Again, the safe flexural strength to be considered in design for PMMs should account for reduction in strength at temperatures exceeding 400 °C. A factor of safety of 2.5 can be considered for SBR and PAE and 1.7 for SIL systems when exposed to temperatures greater than 400 °C.

6.4 Porosimetry results

Porosity and pore size distribution were studied on UCM, SBR and PAE mortars at 10 % p/c dosage, and on silane mortars at 0.25 % e/c dosage. At elevated temperatures, the porosity and distribution of pores were found be significantly altered. The pore size distribution plot of unmodified mortars is presented in Figure 6.4. The UCM had smaller (10 µm to 50 nm) pores than larger pores (20 to 50 µm indicating ITZ). With increasing temperature of exposure, porosity increased in the lower pore sizes up to 400 °C, beyond which it increased in the larger pores as well.

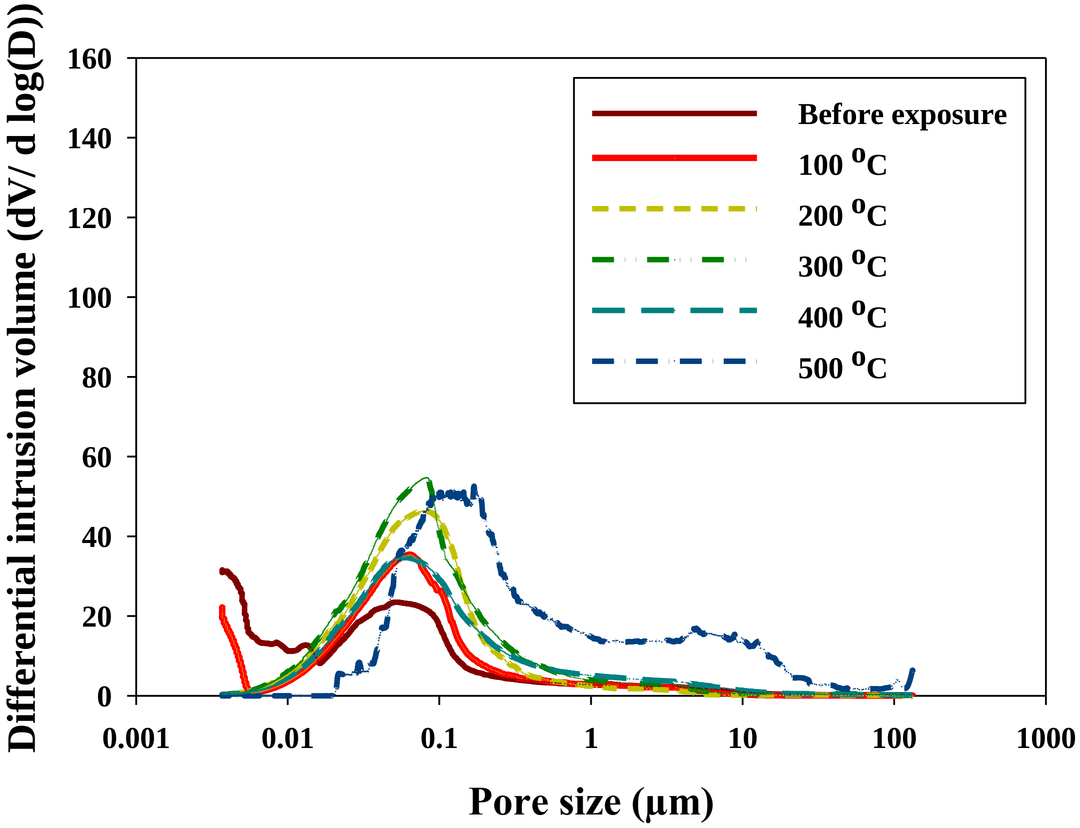


Figure 6.4: Pore size distribution of UCM at elevated temperatures

With SBR mortars, as seen from Figure 6.5, there is significant porosity at both lower and higher pore sizes at ambient and elevated temperatures, with more intruded Vol. in the larger pore sizes. PAE modified mortars experienced a coarsening effect in the pores with the Vol. increasing more in the larger sizes for temperatures exceeding 200 °C, as seen in Figure 6.6. The silane modified systems showed lesser porosity at all elevated temperatures among the PMMs (see Figure 6.7), with the porosity increasing for temperatures greater than 300 °C, more at the larger pore sizes.

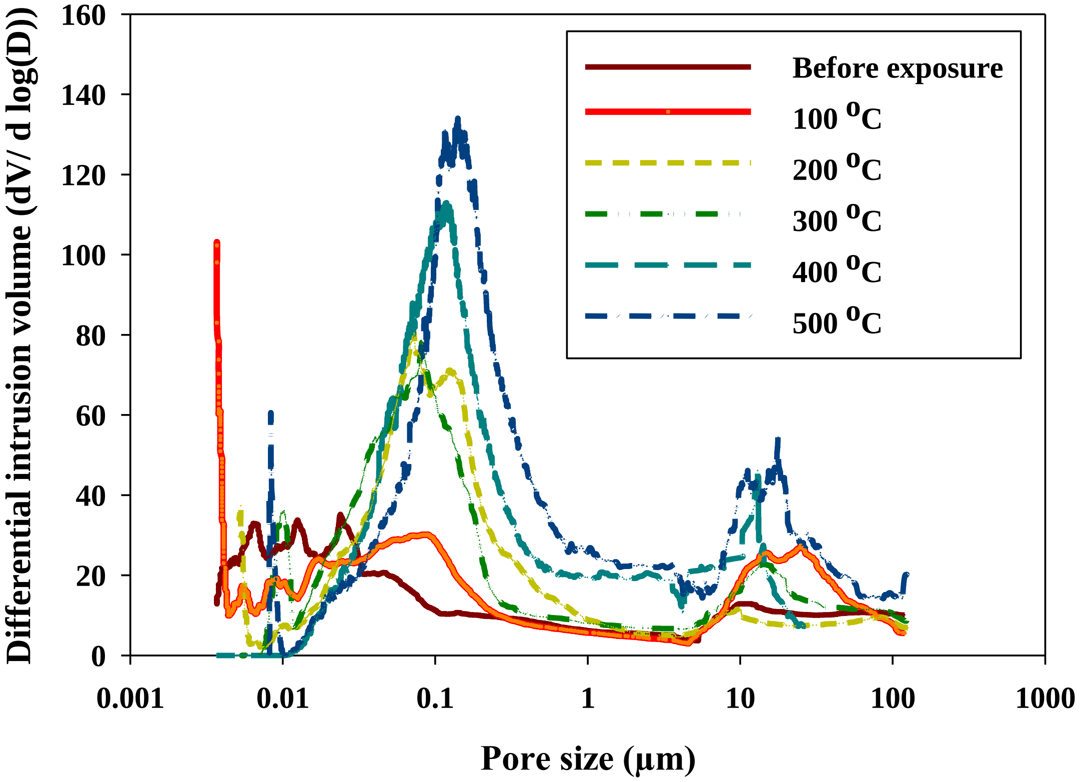


Figure 6.5: Pore size distribution of SBR modified mortars at elevated temperatures

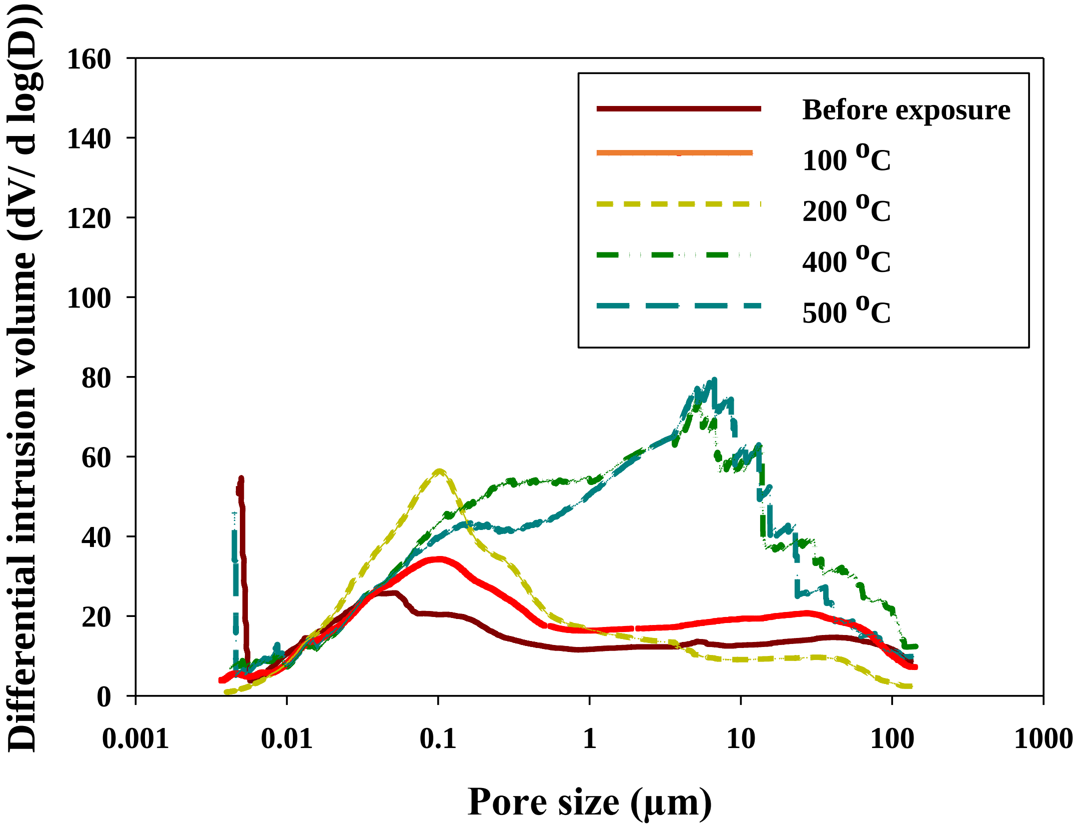


Figure 6.6: Pore size distribution of PAE modified mortars at elevated temperatures

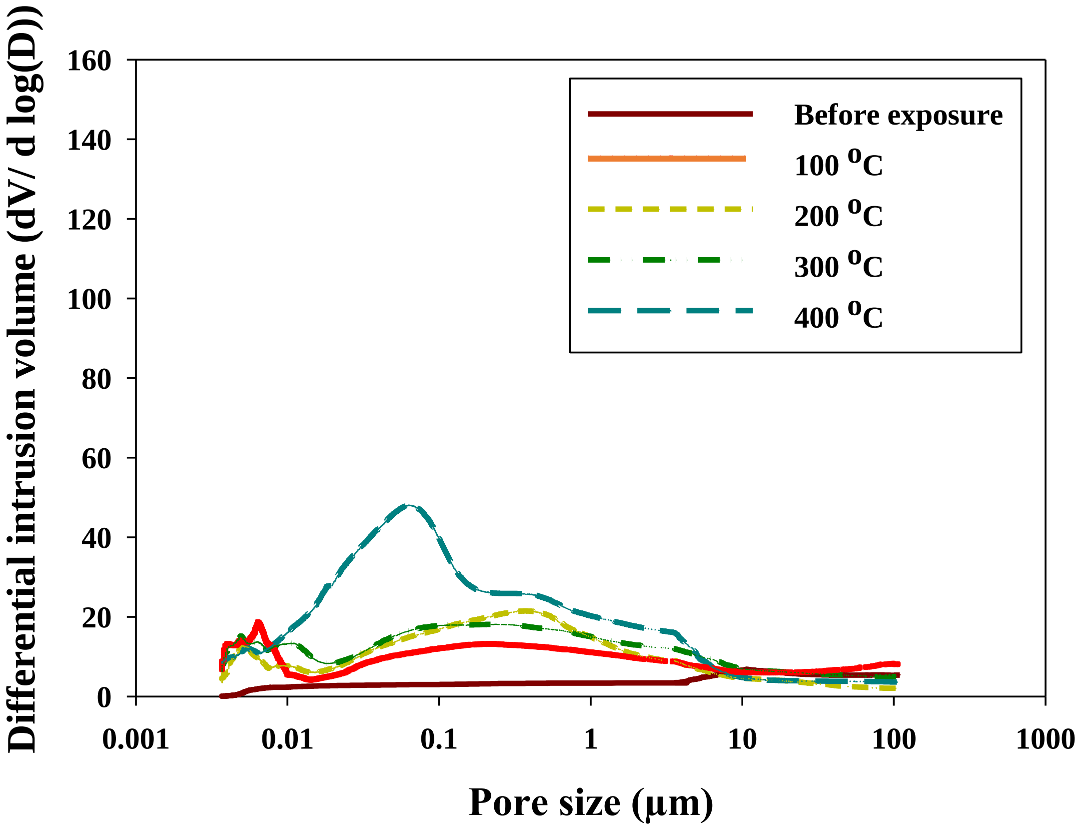


Figure 6.7: Pore size distribution of silane modified mortars at elevated temperatures

Considering porosity in terms of cumulative intruded volume in the sample, before exposure to elevated temperature conditions, the porosity, from Figure 6.8, of the silane mortars was found to be lower than that of UCM, whereas SBR and PAE mortars showed higher porosity. The porosity increased with temperature for both UCM and all PMMs, with the increase being higher in the PMMs. All PMMs except PAE, showed a rapid increase in porosity when heated beyond 300 °C. Silane mortars showed a relative increase in porosity with UCM up to temperature of 300 °C, beyond which it increased drastically. Silane modified systems experienced lower porosity among all the PMMs at all elevated temperatures.

From the cumulative volume of porosity (see Figure 6.8) in the various PMMs at elevated temperatures (also presented in Table 6.3), the porosity results were in good agreement with the mechanical properties tested after exposure to elevated temperatures, where the strengths dropped below 50 % of the strength at ambient conditions with a drastic increase in porosity, for temperatures exceeding 300 °C. Polymeric systems of SBR and PAE suffered a progressive increase in porosity when temperature was increased, with a greater increase in porosity levels for temperature exceeding 300 °C. Silane mortars had a lower increase in porosity with an increase in temperature as the UCM. The porosity developed in SBR and PAE systems was about 100 % higher than that in the silane mortars.

Table 6.3: Cumulative porosity in UCM and PMMs after subjected to elevated temperatures (MIP data)

Temperature (°C)	Mortar system	Porosity (mm^3/g)
Room temperature	UCM	48
	SBR 10 % p/c	62
	PAE 10 % p/c	74
	SIL 0.25 % e/c	47
100	UCM	46
	SBR 10 % p/c	72
	PAE 10 % p/c	88
	SIL 0.25 % e/c	43
200	UCM	50
	SBR 10 % p/c	89
	PAE 10 % p/c	95
	SIL 0.25 % e/c	40
300	UCM	58
	SBR 10 % p/c	94
	PAE 10 % p/c	105
	SIL 0.25 % e/c	43
400	UCM	62
	SBR 10 % p/c	117
	PAE 10 % p/c	114
	SIL 0.25 % e/c	42
500	UCM	68
	SBR 10 % p/c	152
	PAE 10 % p/c	120
	SIL 0.25 % e/c	41

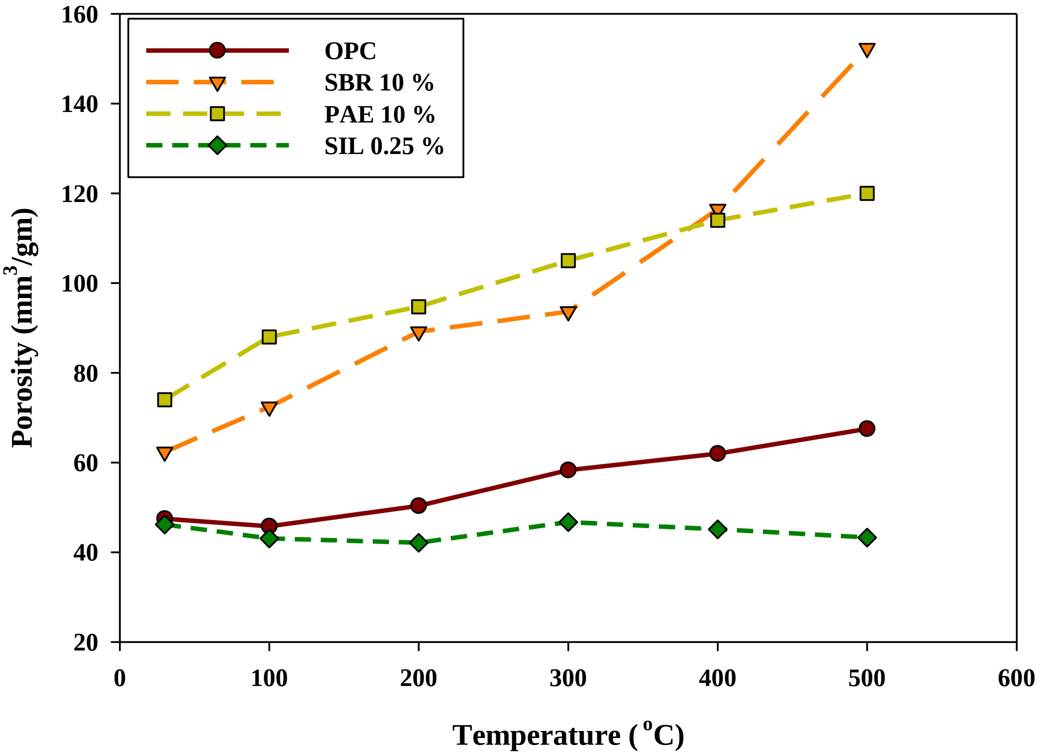


Figure 6.8: Porosity of UCM and PMMs developed at various temperatures

The higher porosity in SBR and PAE mortars when exposed to temperatures beyond 300 °C, is due to the release of vapourized polymer, thereby reducing the risks of spalling. The porosity developed in UCM and silane mortars was much lower than that in conventional polymeric systems, such as SBR and PAE. The increase in porosity for the UCM and silanes was found to be less than 10 %, even at a temperature of 400 °C. The higher retention of strength with the silane mortars is on account of the lower reduction in porosity of the systems.

It is also seen that the trends of the porosity in the various polymeric systems are in accordance with those of the mechanical properties, with an increase in porosity on exposure to elevated temperature corresponding to a drop in strength. Correlation of porosity and compressive strength of SBR, PAE and SIL systems at various elevated temperatures is presented in Figure 6.9, Figure 6.10 and Figure 6.11, respectively. From the plots of SBR and PAE polymeric systems, it is seen that the drop in compressive strength with a rise in exposure temperature is the same or greater than the rate of increase of porosity at these exposure conditions. However, in the SIL systems, the drop in compressive strength is marginal even though there is an increase in porosity at elevated temperatures. As the increase in porosity of SBR and PAE polymeric systems results in a significant decrease in compressive strength, the incorporation of such polymers in mortars that have to withstand high temperatures has to be done with caution. SIL systems are to be preferred more when better retention of strength is required when exposed to higher temperatures.

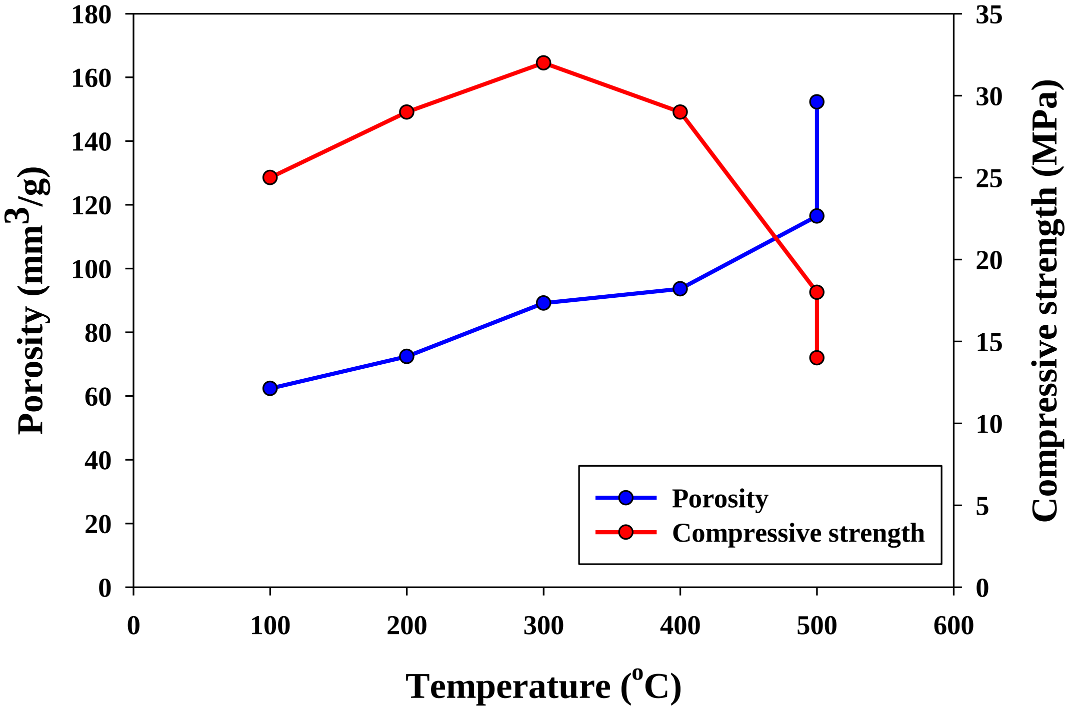


Figure 6.9: Porosity and strength trends of SBR modified polymeric systems at elevated temperatures

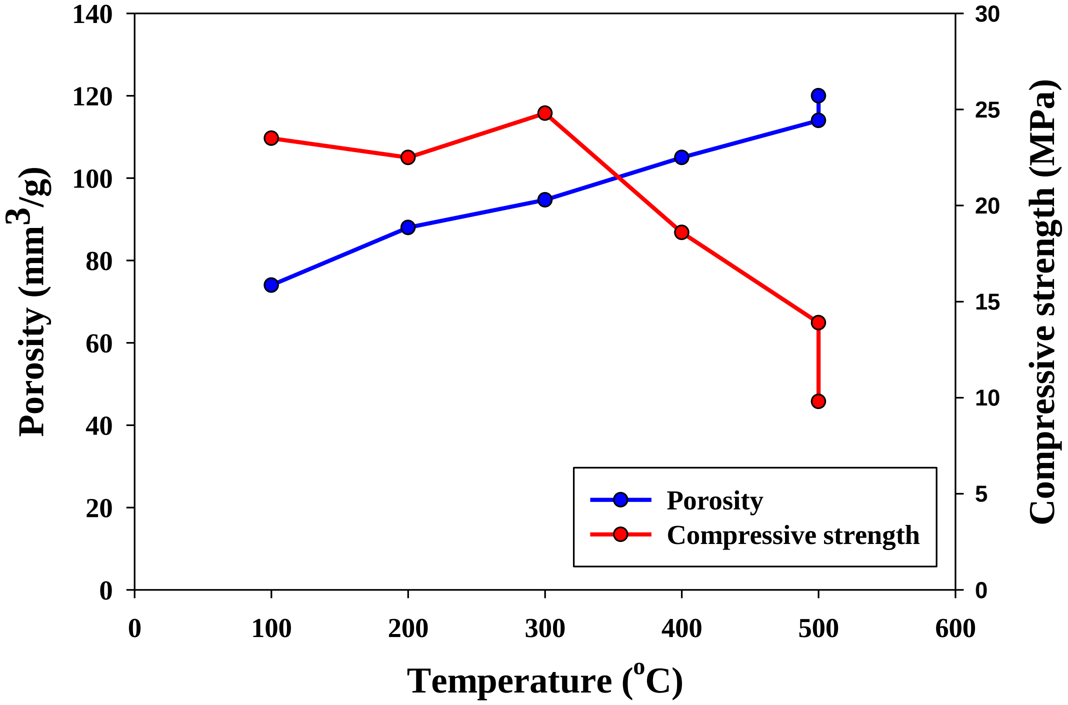


Figure 6.10: Porosity and strength trends of PAE modified polymeric systems at elevated temperatures

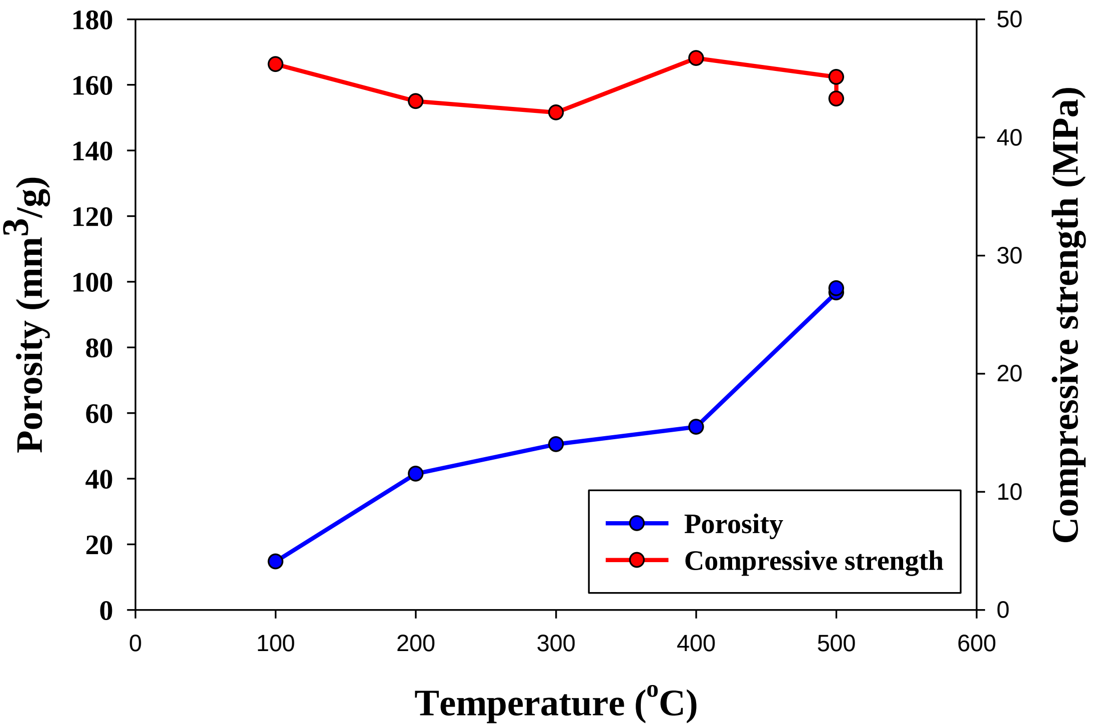


Figure 6.11: Porosity and strength trends of SIL modified systems at elevated temperatures

6.5 XRD studies

From the XRD studies on various polymeric systems subjected to elevated temperatures, the deterioration was similar to that in the UCM. No phase change of polymers was noticed in the XRD data obtained. Polymeric systems of SBR and PAE showed similar properties on exposure to elevated temperatures, with the counts (representative of the intensity of X-ray) of calcite increasing (indicated by CC at 2θ values of 24 ° and 30 °; Snellings et al. 2014) and that of portlandite decreasing (indicated by CH at 2θ values of 18 °and 34 °; Snellings et al. 2014), with a rise in temperature as seen from Figure 6.12. The increase in calcite may be due to the open heating in the muffle furnace where the calcium hydroxide gets carbonated to calcite in the presence of optimal moisture in the mortar (Muthadhi and Kondharaman 2014). Decomposition of portlandite was also seen beyond 300 °C. The intensity of alite and belite phases were found to decrease (2θ of 32 °; Snellings et al. 2014) above 300 °C along with the deterioration of calcium silicate gel in the same 2θ angle range. The reduction of strength in polymer modified mortars beyond 300 °C can be attributed to the deterioration of calcium silicate hydrate phases along with the portlandite phase. In silane modified mortars, except for the C_3S and C_2S phases present up to temperatures of 500 °C, the compositional properties were similar to other polymeric systems. Silanes have been reported to be used in composites to improve the cross-linking of polyethylene polymer composites and hence provide higher thermal stability (Poostforush et al. 2016). The high thermal stability of silane due to the Si-O-Si bonds, make alkoxy silanes non-combustible (Biggs 1993). It is known that the silanol groups, formed by the hydrolysis of silane get adsorbed on the cement grains and the hydration products. This effect of silanes is attributed to the comparable presence of C_3S and C_2S phases even at higher temperature up to temperature of 500 °C. as the sampling was done on mortars with relatively larger amount of crushed aggregates, the other predominant peaks in the XRD plot (2θ of 21, 26, 27, 36, 39, 43, 48) indicates quartz peaks (Angyan et al.1999).

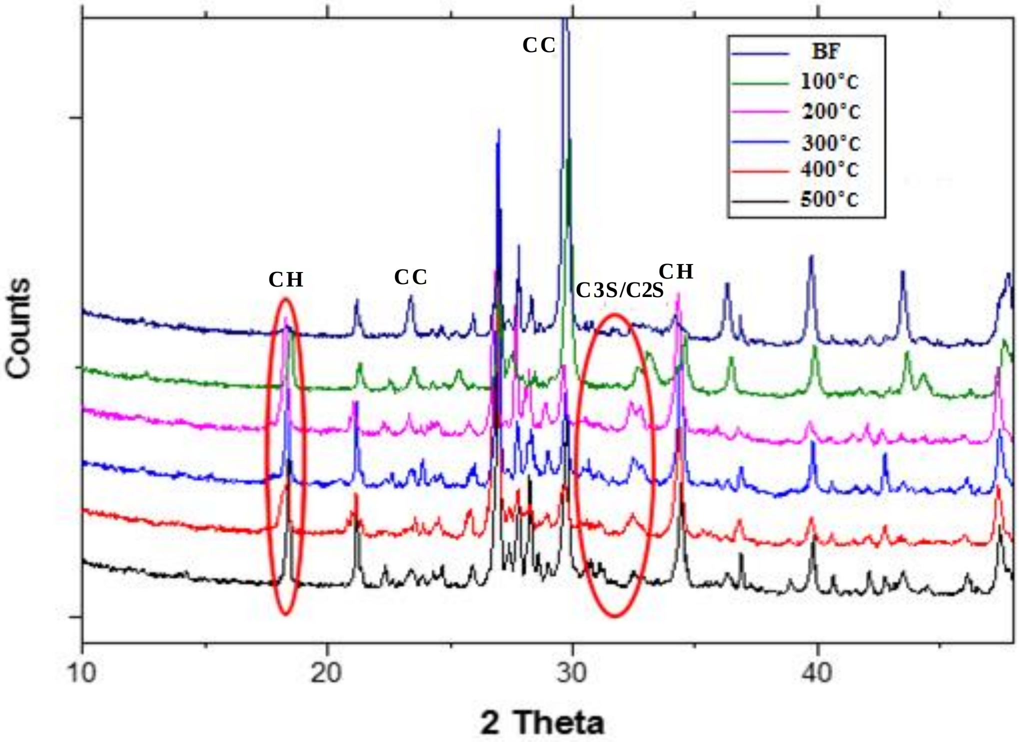


Figure 6.12: XRD results on SBR modified mortars at 10 % dosage after exposure to various temperature conditions

CH- calcium hydroxide (portlandite); CC – calcium carbonate (calcite); C_3S – alite phase (tricalcium silicate); C_2S – belite phase (dicalcium silicate)

6.6 Discussion

The mechanical properties of PMMs were found to increase initially when exposed to temperatures up to 100 °C due to the formation of additional CSH as seen from the XRD results plotted in Figure 6.8. The strengths retained were found to be lower than 50 % beyond 300 °C, thereby identified as a critical temperature for the exposure of polymer modified systems. Deterioration of portlandite, alite and belite phases were noticed for temperatures exceeding 300 °C from the XRD results, which explains the retention of less than 50 % of the strength above such temperatures.

Compared to the SBR and PAE systems, silane modified mortars showed higher retention in strengths at all temperatures. The porosity level in silane PMMs was comparable with the UCM. The high thermal conductivity of silane groups adsorbed over the silicate rich phases (alite, sand) in conjunction with the thermal stability of Si-O-Si bonds, providing protection to the cementitious compounds, thereby imparts higher retention of strength and density. It is also noted that the degree of crystallinity (indicated by sharper peaks in the XRD spectra) of polymers used in the study decreases progressively in the order of silanes > PAE > SBR. Thermal properties of crystalline and semi-crystalline polymers are mainly characterized by their melting point and that of amorphous polymers depend on the glass transition temperature (Santos et al. 2013). The lower retention of properties seen with exposure to higher temperature ranges in SBR and PAE mortars can be accounted by the lower melting point of these polymeric systems. The retention of properties after exposure to higher temperature conditions was seen to be improved with silane mortars due to the relatively higher transition temperature of the silane systems (Young and Lowell 2011).

Coarsening effect of pores were seen in PAE mortars where the Vol. of larger pores increased when exposed to temperatures beyond 300 °C. With SBR and silane polymers, the pore Vol.s consistently increased for the larger and smaller pore sizes, with the temperature of exposure, resulting in a rapid increase of Vol. in the smaller pore sizes, which is less critical in influencing the water permeability and strength aspects, thereby making them more suitable for applications where durability is critical.

Thus, to account for the reduction in strength and increase in porosity at elevated temperature conditions in systems where polymer modifiers are used, a lower design strength should be taken to account for exposure above 300 °C for safe functionality.

6.7 Summary

This chapter discusses the properties of polymer modified mortars exposed to elevated temperature conditions (up to 600 °C). Behaviour is assessed based on the mechanical properties, porosity and pore size alterations when exposed to conditions of high temperatures. The deterioration of the systems was assessed using XRD. The following results have been inferred from the test results obtained:

(i) The compressive and flexural strengths of mortars were found to initially increase up to temperature of 200 °C beyond which they reduce. Thus, a lower strength than that at normal temperatures should be considered in design for exposures greater than 300 °C.

(ii) The increase in porosity of various PMMs at elevated temperatures varied with the pore sizes. The PAE mortars exhibited an increase in larger pores at higher temperature (coarsening effect) while SBR and silane mortars showed an increase in both smaller and larger pores.

(iii) The deterioration of various compounds (portlandite, alite and belite phases) were seen in all PMMs beyond 300 °C.

CHAPTER 7

PERFORMANCE EVALUATION OF POLYMER MODIFIED MORTARS UNDER FIRE

7.1 Introduction

Fire damage, despite being a severe jeopardy in any type of building, is often given little importance in terms of material selection for repair. A major requirement of any material used in construction should be its fire safety, in addition to structural integrity, so that the combustibility and flammability at such conditions is in control and that it does not add to the toxicity level of the atmosphere when a fire breaks out. Combustibility and flammability of building materials can be tested in accordance with the ASTM E 136, ASTM E 84, and ASTM E 119 standards. Polymer modified mortars being widely used in many civil constructions should be evaluated to assess the performance in a fire.

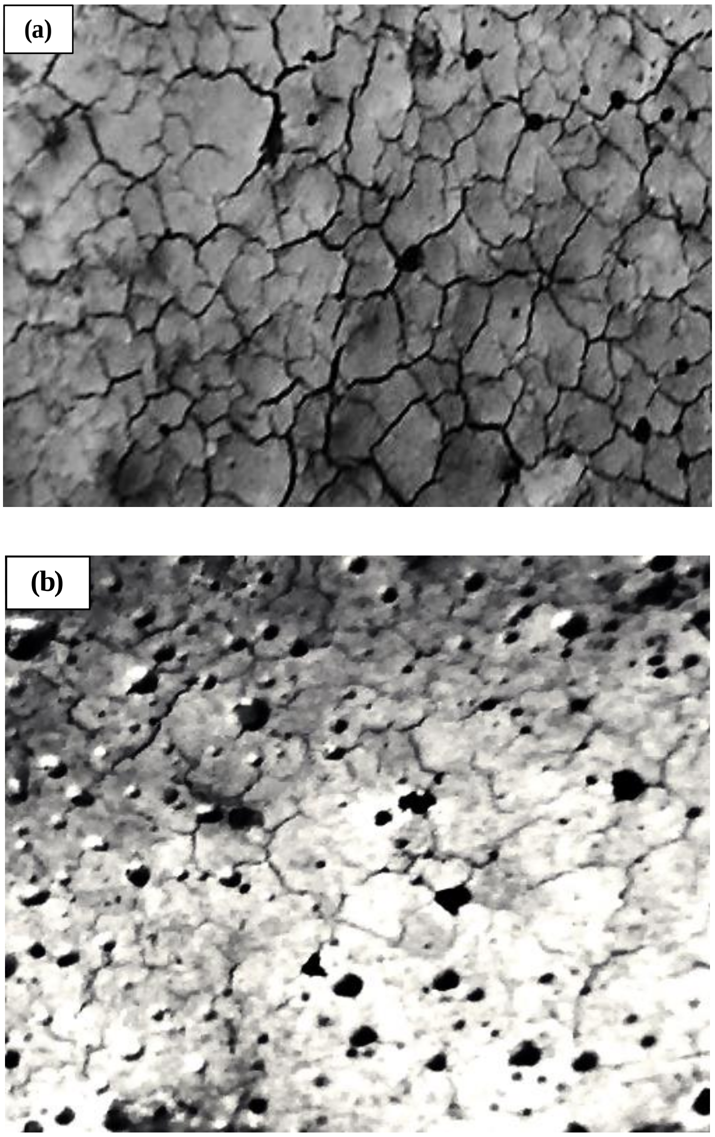
This chapter discusses the response of various PMMs exposed to fire conditions (maximum temperature of 1000 °C), evaluated based on combustibility and flammability by visual inspection.

7.2 Experimental procedure

The combustibility is tested as per ASTM E 136 where the specimen is positioned in a furnace heated to 1000 °C and placed until the thermocouple reading has stabilised. After 1 hour of exposure to fire conditions, the specimens are cooled to room temperature and subjected to visual examination of face deterioration. The material is considered non-combustible if it satisfies the weight loss is not greater than 50 % and no flaming is observed when maintained at 1000 °C for an hour. Mortars of PMMs modified with SBR (10 % p/c), PAE (10 % p/c) and SIL (0.25 % e/c), after being cured in Type 2 curing (i.e., 7 days of moist curing followed by air curing up to 28 days of age), were subjected to fire conditions in the furnace.

7.3 Results of testing under fire conditions

The combustibility and flammability of the various PMMs as observed are reported in this section. Using the criteria mentioned above, all the mortars were concluded to have no combustibility and flammability. However, differences were seen on the surface of the different polymeric systems in terms of the extent of cracking, as evident from Figure 7.1. The UCM showed cracking but a less porous surface was generated when compared to the PMMs. SBR and PAE mortars had highly porous surfaces after the exposure, which may be due to the melting of the polymers used that led to the release of internal pressure with lesser cracking on the surface. Silane mortars also showed a porous surface with exposure to elevated temperatures.



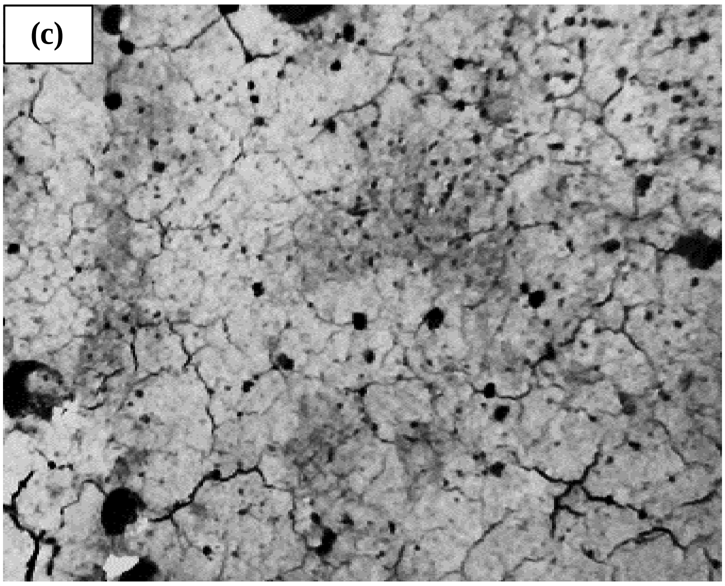


Figure 7.1: Mortar surfaces after exposure to fire conditions at 1.5x magnification (a) UCM (b) PAE and (c) silane

As expected, no strength is retained in any of the mortar systems after being subjected to fire conditions.

7.4 Discussion

As seen from Figure 7.1, introduction of polymers resulted in a more porous surface when subjected to fire conditions. The highly permeable surface on exposure to fire conditions seen with polymeric mortars can be on the account of the higher thermal conductivity of these polymeric systems than the UCM, where a relatively more cracks are found to develop with lesser pore surfaces. Owing to the higher porosity formed in polymeric systems in a fire, channels can be formed for the release of gas pressure, thereby reducing the risk of spalling when compared to UCM.

7.5 Summary

From the assessment of polymeric systems on exposure to fire conditions, the following results were inferred.

(i) Performance of mortars in fire conditions is influenced by the incorporation of polymers.

(ii) All the mortars (UCM and PMMs) satisfied zero combustibility and flammability, up to temperatures of 1000 °C.

(iii) Polymeric systems showed highly porous surfaces with less cracks than in the unmodified mortars.

CHAPTER 8

CONCLUSIONS AND SCOPE FOR FURTHER STUDIES

8.1 Introduction

In this study, the influence of curing, dosage and various exposure conditions, on the performance of polymer modified mortars was investigated. The scope of this study consisted of assessing mortars with the dosages of polymers generally recommended, curing types commonly employed at field and the exposure conditions to which the systems can be possibly exposed to, considering a range of applications.

This Chapter presents the major conclusions and recommendations inferred from the study, and the scope for further research in the area of polymer modifications in cementitious systems.

8.2 General conclusions

Incorporation of polymers into a cementitious system impacts both the mechanical properties and durability aspects (including shrinkage properties and resistance to external agents). Within the scope defined, the dosage, curing type and exposure conditions are found to influence the properties of cementitious system. The properties of all the polymeric systems are found to be dependent on the curing type, with higher sensitivity of the SBR and PAE systems and lesser variation in silane systems. At normal conditions of testing, among all PMMs, mechanical properties are higher in the silane modified mortars; while SBR modified mortars experienced lower shrinkage and permeability.

For all polymeric systems, limited wet curing (7 days) followed by air curing is found to yield higher mechanical properties. Shrinkage is also improved with limited wet curing and increases progressively when longer wet curing is provided. Water permeability results are, however, found to benefit more with extended wet curing periods (i.e., 28-day wet curing), where lower depth of penetration of water is attained than with limited wet curing (i.e., 1 and 7 days). Microstructural studies on polymeric systems using SEM validate the test results obtained, with pronounced presence of hydrates (which leads to localization of polymer film formation) seen in longer wet curing periods (i.e., 28-day wet curing) and shorter periods of wet curing (i.e., 1 and 7 days) resulting in a more uniform surface conducive for the formation of a continuous polymer film. The surface morphologies of silane modified mortars shows marginal changes with various curing types, for which most of the properties are less dependent on curing conditions. It is also noted that employing higher dosages of polymers did not favour PAE mortars as for SBR mortars. The leaching of polymers seen at dosages of PAE results in higher shrinkage and water permeability for the mortars.

On exposure to accelerated conditions of weathering, the performance followed the order of SIL > PAE > SBR in all the properties. The retention of properties seen with aging in silane mortars makes it an excellent choice for outdoor applications such as plastering and overlays, and SBR due to the lower shrinkage and water permeability among all PMMs, can be recommended for interior applications such as floorings in washrooms. Ageing due to weathering is found to adversely affect the water permeability of the polymeric systems more critically than the mechanical properties and shrinkage. The water permeability of SBR mortars after exposure to accelerated weathering experienced a four-fold increase in the depth of penetration of water, particularly when higher dosages are used. Mechanical properties are favoured more with longer wet curing periods (28-day), while lower shrinkage is attained with limited wet curing periods (1 or 7- day) followed by air curing.

On exposure to elevated temperatures, the PAE mortars exhibit an increase in porosity of the larger pores at higher temperature (coarsening effect) while SBR and silane mortars suffered an increase in porosity for both smaller and larger pores. Thus, SBR and silane mortars are considered more stable at such exposures of elevated temperatures with less change in porosity in the various pore sizes. Considering a retention of 50 % strength at ambient conditions, the critical temperatures of exposure for SBR, PAE and silane mortars are identified as 300 °C, 400 °C and 500 °C, respectively. All the polymeric systems employed shows zero combustibility and flammability even at 1000 °C.

Considering the primary requirement in various application of PMMs, such as comparable mechanical properties (for overlays), lower water permeability (for water proofing) and lower shrinkage (for repair mortars), the recommendation for the curing conditions for each of the specific application, which can provide the expected performance, is given in Table 8.1 below.

Table 8.1: Recommendation of polymer and curing type for specific applications

Type of polymer	Overlays in floorings	Water proofing	Repair mortar
SBR	7- day wet curing	7- day wet curing	7- day wet curing
PAE	7- day wet curing	1- day wet curing	1- day wet curing
SIL	28- day wet curing	1- day wet curing	1- day wet curing

8.3 Specific conclusions

8.3.1 Workability

(i) Workability of all PMMs is higher than the unmodified system for the same water to cement ratio of 0.45, and further improves with increase in dosage of the polymers.

(ii) Among the PMMs, silane offers higher enhancement of workability than other polymeric systems.

8.3.2 Fresh unit weight

(i) Wet density of cement mortars reduces with the introduction of polymers into the cementitious system making them lighter in weight than the UCM; the lower density being with PAE and higher with silane modified mortars among the PMMs.

(ii) The higher gravimetric air content measured in PAE mortars is accounted for the lower density.

8.3.3 Initial and final setting time

(i) Incorporation of polymers extends the setting time of cement due to the delay in hydration by polymer film formation in SBR and PAE systems.

(ii) However, the setting time of cement paste modified with the silane is lower than that of UCM.

8.3.4 Influence of curing on the performance of PMMs at standard conditions

8.3.4.1 Morphological studies using SEM

(i) The nature of hydrates formed in the PMMs and unmodified mortars are differentiated in SEM studies with the UCM characterized by a coarser and uniform microstructure, and PMMs with an interconnected network of polymer-hydration products with open pores spaces in a dense structure.

(ii) Silane modified mortar has minor differences in the microstructure compared to UCMs, with layers of discontinuous polymer film.

(iii) Microstructure evolution in polymeric systems of SBR and PAE is dependent on the period of curing with 28-day wet curing showing more pronounced presence of hydrates, which leads to localization of polymer film formation; and shorter periods of wet curing (i.e., 1 and 7 days) followed by air curing, showing a more uniform surface conducive for the continuous polymer film to form.

(iv) The compactness of the microstructure due to polymers of SBR and PAE progressively decreases with an increase in the duration of wet curing.

8.3.4.2 Porosity studies using MIP

(i) Curing is found to impact critically on the porosity and pore size distribution of the cementitious system. 1- day wet curing results in more pore Vol. in the size range of 0.05 to 0.5 µm (that impact the strength and permeability), and 7 and 28-day wet curing, possesses higher pore Vol. in the smaller size ranges of 0.005 to 0.05 µm (that influence the shrinkage).

(ii) SBR and PAE mortars shows a varied pore size distribution with the former showing a coarser pore in the range of 10 µm to 100 µm, and PAE in the capillary pore sizes of 1 µm to 10 µm.

(iii) Silane modified systems shows a pore structure similar to that of UCM with negligible porosity in the ITZ and larger pores (10-100 µm), and higher porosity in capillary and gel pore ranges (< 10 µm).

(iv) Porosity level in the conventional polymeric systems of SBR and PAE is about three times than in silane mortars.

8.3.4.3 Compressive strength

(i) Increase in dosage of polymer results in a lower compressive strength for both SBR and PAE mortars due to reduction in gel space ratio by the introduction of polymer.

(ii) SBR and PAE mortars shows higher compressive strength with limited wet curing periods of 1 day and 7 days followed by air curing, where both polymer film formation and sufficient cement hydration occurs as seen in SEM images.

(iii) Silane modified mortars shows higher compressive strength with extended periods of wet curing (28 days) as the UCM. The increase in strength of silane mortars is uniform over the curing conditions from limited to prolonged wet curing periods.

(iv) Influence of curing is found to be more critical in influencing the compressive strength of PAE mortars, than in SBR and silane mortars.

8.3.4.4 Flexural strength

(i) PMMs shows similar increments and decrements in flexural strength as in compressive strength at various curing types.

(ii) For SBR and PAE modified systems, at lower dosages of polymer (4.5%), 7- day wet curing yields higher flexural strength.

(iii) When higher dosages of polymer are used (10 %), flexural strength is improved in systems with limited periods of wet curing (1-day) due to greater binding of the components in the cementitious system by the polymer film.

(iv) Flexural strength of PAE mortars is noted to be higher than the SBR due to higher carboxylic content imparting better flexibility in the former.

(v) PAE mortars shows no improvement in flexural strength with increase in dosage, on contrary to SBR where enhancement of flexural strength is seen in higher dosages with limited periods of wet curing (1-day wet curing).

(vi) When the polymer content is higher, the mortar could have higher flexural strength when the wet curing is limited to 1 to 7 days.

(vii) Silane polymeric systems are less dependent on various curing conditions on contrary to SBR and PAE systems with higher sensitivity to curing. Silane modified mortars shows higher flexure with 7 days of wet curing (Type 2) with marginal differences among various curing types.

8.3.4.5 Total drying shrinkage

(i) In polymeric systems of SBR and PAE, the shrinkage strain is higher with longer durations of wet curing due to the possibility of higher amount of water in the capillary pores.

(ii) Longer periods of wet curing (28 days) results in higher shrinkage strain in PAE systems than in SBR systems due to higher porosity of PAE mortars along with more of smaller pore sizes (as identified from MIP).

(iii) Longer durations of wet curing greater than 7 days yields higher shrinkage strain in PAE mortars than in other systems.

(iv) Silane mortars shows lower shrinkage strain even with longer periods of wet curing and with lesser sensitivity to curing duration than other PMMs.

(v) Sensitivity of shrinkage strains of polymeric systems based on the period of wet curing follows the order of PAE > SBR > silane systems.

(vi) SBR mortar shows lower shrinkage with limited wet curing periods among the PMMs, hence, suitable for applications without adequate curing.

(vii) For systems with prolonged wet curing conditions being obligatory, silane polymeric systems, which has lower shrinkage strain at such conditions, can be recommended.

7.3.4.6 Water permeability

(i) SBR mortars shows lower depth of penetration of water than the UCM while silanes gave comparable permeability with the unmodified mortars.

(ii) PAE mortars offers higher depth of penetration at all curing types and dosages due to the leaching of polymer and high gravimetric air content associated with higher dosages of acrylic based polymer.

(iii) The depth of penetration of water in SBR mortars reduces when longer wet curing periods (28 days) are provided; whereas, PAE mortars shows lower depth of penetration at shorter wet curing periods (1 days and 7 days).

(iv) The water permeability results of silane mortars are similar for all curing durations, showing lesser effects due to curing in these systems.

8.3.5 Influence of curing on the performance of PMMs after exposure to weathering conditions

8.3.5.1 Compressive strength

(i) Ageing is found to impact polymer additions positively only for silane mortars subjected to shorter periods of wet curing of 1-day. All other polymeric systems show a loss of properties on exposure to accelerated weathering when compared to the unmodified mortar subjected to similar conditions of aging.

(ii) Strength of PMMs is higher for specimens with longer periods of wet curing (28 days) due to limited polymer film formation than in limited duration of wet curing, which could explain the lower degradation of strength.

(iii) PAE systems with limited wet curing (1 to 7 days) retains the strength and specimens with longer wet curing periods (28 days) shows an increase in compressive strength.

(iv) Higher reduction in strength is reported in SBR mortars at all dosages particularly when subjected to limited period of curing (1-day wet curing).

(v) Silanes mortars shows an increase in compressive strength independent of the curing types.

8.3.5.2 Flexural strength

(i) Retention or increase in strength is seen with curing type that follows longer wet curing periods (28-day wet curing) as in compressive strength results. However, flexural strength retention is also seen with limited periods of wet curing in SBR and silane mortars.

(ii) The SBR and silane polymeric systems shows an increase in flexural strength on aging, for all curing types. While the PAE systems suffers a loss in the flexural strength at all dosages and curing conditions.

(iii) The performance of silane mortars improves when longer wet curing periods are provided with no reduction in strength for any curing type after exposure to accelerated conditions of weathering.

8.3.5.3 Total drying shrinkage

(i) The shrinkage evaluation carried out after the accelerated weathering shows a higher shrinkage for specimens with 28-day curing than in systems subjected to lower wet curing periods (1 and 7 days).

(ii) The shrinkage strain of PMMs are lower with aging than the shrinkage strain obtained after 28 days with the effect of aging having lesser influence on shrinkage in all polymeric systems, except for 10 % SBR systems with limited wet curing period (1 and 7 day).

(iii) The shrinkage strain of all PMMs subjected to weathering is higher than the UCM exposed to similar conditions with no positive effects of polymer addition seen for all PMMs except for silane mortars subjected to 1-day wet curing.

8.3.5.4 Water permeability

(i) Permeability of all PMMs are found to be higher than UCM after exposure to accelerated weathering.

(ii) Among the PMMs, SBR and silane shows lower depth of penetration of water with dependence on curing type. However, water permeability of silane mortars remains similar at all curing conditions, in contrast with other polymeric systems.

(iii) PAE and silane mortars has lower penetration of water after accelerated weathering at all dosages and curing conditions, signifying an improvement in performance with the exposure.

(iv) SBR modified systems shows an increase in water permeability after exposure to accelerated weathering conditions signifying a deterioration of these systems during their service in exterior applications.

8.3.6 Performance evaluation of polymer modified mortars at elevated temperatures

8.3.6.1 Compressive strength

(i) UCM and silanes retains about 80 % of the strength at ambient conditions for temperatures exceeding 400 °C, whereas SBR modified mortars retains only 60 % of strength and PAE modified mortars 40 %.

(ii) Thus, to account for the reduction in strength at elevated temperatures in systems where these polymer modifiers are used, a lower value of strength is to be considered in the design for temperatures exceeding 300 °C (for SBR), 200 °C (for PAE) and 500 °C (for SIL).

(iii) The compressive strength of UCM shows a marginal increase when exposed to temperatures up to 400 °C (as a result of hydration of the unhydrated cement grains at these elevated temperatures) and subsequent reduction in strength when heated further (on account of the decomposition of $Ca(OH)_2$ occurring above 400 °C).

(iv) The PMMs exhibits an initial decrease in strength when heated to 100 °C followed by a gain in strength at 200 °C.

(v) The SBR modified mortar shows a more pronounced drop in strength up to 100 °C; and above 300 °C, the strength continuously reduces.

(vi) Among the PMMs tested, silane modified mortars behaves similar to an unmodified mortar with no sharp decrease in strength even when exposed to temperatures up to 500 °C and shows the highest retention of compressive strength.

8.3.6.2 Flexural strength

(i) A significant improvement in flexural strength values is seen for all PMMs on exposure to temperatures up to 300 °C except SIL. However, above this temperature there is an evident loss of strength.

(ii) The flexural strength of UCM is not significantly influenced by the temperature increase up to 400 °C, above which it reduces; and for SIL modified mortars, a marginal decrease in strength is seen with each higher temperature with lower decrease in flexural strength among the PMMs at even 500 °C.

(iii) More than 50 % of flexural strength is retained for temperatures exceeding 400 °C for both SBR and PAE mortars and about 70 % is retained for silanes, for which the safe flexural strength to be considered in design for PMMs should account for the reduction at temperatures exceeding 400 °C.

8.3.6.3 Porosimetry studies

(i) The porosity increases with temperature for all PMMs and UCM but the increase being higher in the polymer modified mortars than in the unmodified systems.

(ii) The UCM has more porosity in the smaller (10 µm to 50 nm) pores than the larger (20 to 50 µm indicating ITZ). With increasing temperature of exposure, porosity increases in the lower pore sizes up to 400 °C, beyond which, it increases in the larger pores as well.

(iii) SBR mortars shows porosity in both lower and higher pore sizes at ambient and elevated temperatures, with more intrusion Vol. in the larger pore sizes.

(iv) PAE modified mortars shows coarsening effect of pores with higher Vol. in the larger sizes for temperatures exceeding 200 °C.

(v) The silane modified systems shows lesser porosity at all elevated temperatures among the PMMs with porosity increasing for temperatures greater than 300 °C, more at the larger pore sizes.

(vi) The porosity developed in UCM and silane mortars are much lower than in conventional polymeric systems such as SBR and PAE. The increase in porosity for the UCM and silanes is found to be less than 10 % even at a temperature of 400 °C. The higher retention of strength with the silane mortars is on the account of the lower reduction in porosity of the systems. However, the lower porosity increases the risk of spalling due to internal accumulation of internal pressure in the systems

8.3.7 Performance evaluation of polymer modified mortars at fire conditions

(i) All the mortars show zero combustibility and flammability when tested.

(ii) UCM shows cracking but with lesser porous surfaces than the PMMs.

(iii) SBR and PAE mortars are characterized by porous surfaces on exposed to fire conditions which may be due to the melting of the polymers that led to the release of internal pressure with less cracking on the surface.

8.4 Scope for further studies

(i) From the studies done in this thesis, it is seen that air entrainment encountered with higher dosages of polymer results in loss of properties which is to be addressed. Impact of suitable anti-foaming agents with the PMMs can be studied to investigate if it influences positively in retaining the beneficial effects of polymer addition.

(ii) The toughness of the polymer modified systems can be tested to evaluate on the bridging of micro-cracks and prevention of crack propagation.

(iii) The synergic effect of employing light weight aggregates and the polymers used in this study for better resistance against fire conditions can be studied.

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APPENDIX A

PERFORMANCE ASSESSMENT OF FIRE RESISTANT COATINGS AND MORTARS

A.1. Introduction

Various temperature resistant coatings and mortars have been marketed in the construction industry for fire protection in civil structures. Urea, silicone and polymeric based products are most commonly used for this purpose. Many of these mortars are marketed as ready-made products to which only water has to be added for obtaining the required workability.

This Annex investigates the response of some fire resisting coatings and mortars commonly employed in order to complement the work presented on PMMs in Chapter 7. Visual inspection of the deteriorated mortars, along with an assessment of mechanical properties have been carried out.

A.2. Products used for the study and methodology for testing

Polyurea and silicone based coatings, and three polymeric fire resistant mortars have been chosen for the study. The products recommended to be used as coatings were applied with uniform thickness over 50 mm cubes of ordinary cement mortar (UCM). As polyurea is a heated plural component application, it cannot be coated over a substrate by normal brushing, for which the ordinary cement mortar specimens were cast and transported to the manufacturer where the polyurea coating of 1 mm thickness was applied using a glass-craft spray machine. For silicone based coatings over the ordinary mortar, a primer coating was applied, after the drying of which the silicone was coated as a thin film.

The evaluation of the fire resisting mortars was done on the 50 mm cubes cast by adding water to the dry mortar to get required consistency. Details of the 3 polymer based fire resistant mortars are given in Table A.1.

Table A1: Polymeric fire resisting mortars used for the study

Mortar	Mortar ID	Water added (% by weight of mortar)
Product with Poly-acrylo-nitrile (PAN) fibres	F1	12 % - 14 %
Structural repair mortar with selected polymer fibres	F2	19 % - 21 %
Product with selected resins	F3	22 % - 24 %

The coated specimens and fire resistant mortar specimens were placed in a muffle furnace where they were subjected to temperatures from 100 °C to 1000 °C, for a period of an hour. Both the polyurea and silicone coatings were tested on the 7th day after coating, for adequate development of strength. Polymeric mortars cast were placed in the furnace for fire testing after 7 days of wet curing, which is the commonly adopted curing practice for most construction projects in India.

A.3. Assessment of performance of coatings and mortars at elevated temperatures

(i) Polyurea coatings

The polyurea coating was found to resist temperatures up to 600 °C, thereby providing good protection to the substrate over which it is applied. At temperatures greater than 200 °C, the coatings were found to bulge (see Figure A1 (i)) and at temperatures greater than 600 °C, the coatings were found to deteriorate with discolouration of the coating and tears at some locations (see Figure A1 (ii)). The coating completely deteriorated when exposed up to 1000 °C, exposing the substrate where (Figure A1 (iii)).

(i)

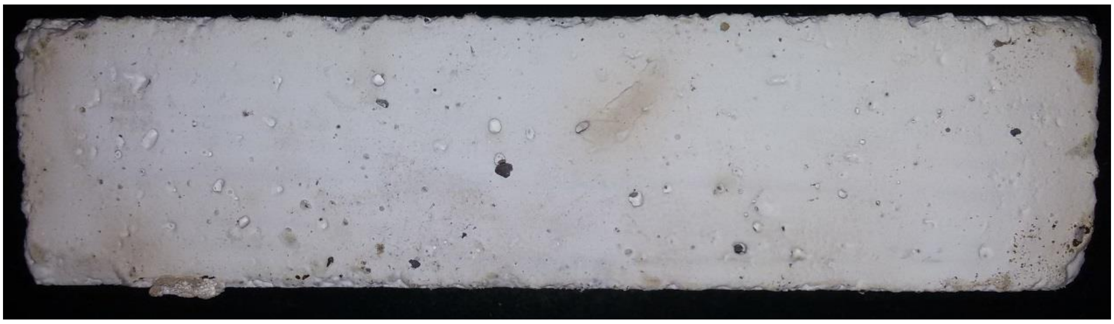
(ii)

(iii)

Figure A1: Polyurea coating after exposure to temperatures of (i) 200 °C (ii) 800 °C and (iii) 1000 °C

(ii) Silicone coatings

Silicone coatings showed lower resistance to elevated temperatures with the coating peeling off at temperatures exceeding 200 °C probably due to the thinness of the coating. The visual appearance of the coatings at various elevated temperatures is seen in Figure A2 below.



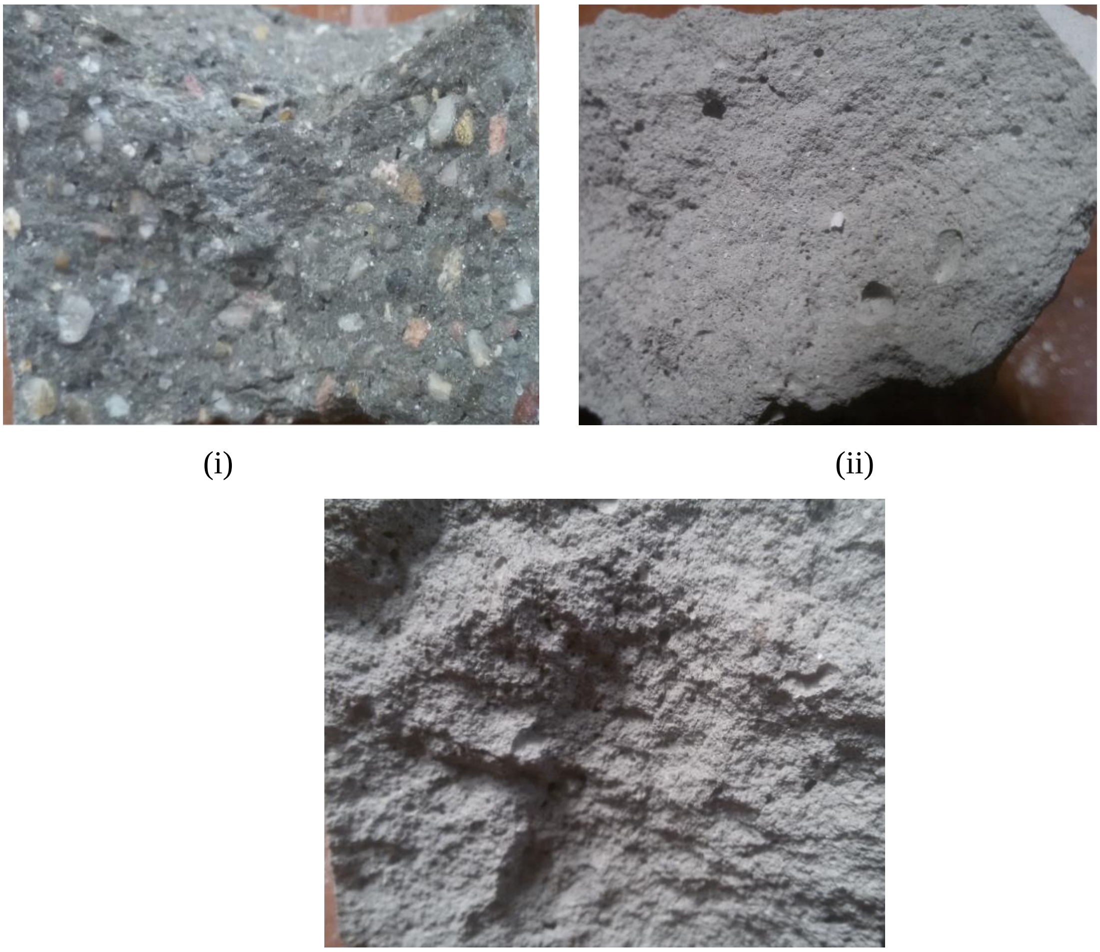
(i)

(ii)

Figure A2: Silicone coatings at (i) 200 °C and (ii) 300 °C

(iii) Fire resistant mortars

Product with Polyacrylonitrile (PAN) fibres (F1): The mortar offered good resistance to temperatures up to 500 °C with no cracks or defects being formed on the surface. However, when tested to temperatures of 1000 °C, the specimens failed completely by rupturing. The mortar had a high compressive strength of 97 MPa before subjecting to elevated temperature conditions, about 28 % of which was retained after exposure to 500 °C. Strength being indicative of the integrity, these mortars are found pertinent for the functionality in terms of strength for temperatures up to 500 °C. As seen from Figure A3 below, the interior of the mortars was seen to be intact even after exposure to high temperatures.



(i) (ii)

(iii)

Figure A3: Interior of the mortar samples (i) before exposure to elevated temperature conditions, (ii) after exposure to 500 °C, and (iii) after exposure to 1000 °C

Structural repair mortar with selected polymer fibres (F2): The performance of the F2 mortar was found to be similar to F1 mortar with no cracks on the surface and the interior remaining intact even after exposure to 1000 °C (see Figure A4). However, the mortar possessed lower compressive strength than F1, with a mean strength of 47 MPa at normal conditions. When exposed to 1000 °C, the specimens ruptured.

Product with selected resins (F3): F3 had the lowest compressive strength of 24 MPa among the fire resistant mortars when tested at normal conditions. However, the mortar practically retained all its the strength up to temperatures of 500 °C. Thus, for those applications that need only low strength but good retention at higher temperatures, the usage of F3 mortars would be beneficial. As in the case of the other fire resistant mortars tested, F3 failed to resist the exposure of 1000 °C.

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